

Research Report

WA-RD 404.1
Contaminant Removal in Runoff

**THE RETARDATION OF HEAVY METALS IN STORMWATER
RUNOFF BY HIGHWAY GRASS STRIPS**

by

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EXECUTIVE SUMMARY

Investigations regarding the introduction of contaminants to the aquatic environment through highway runoff began in the late 1970's. Interest in this area of study has continued to increase, particularly in the area of design, operation, and effectiveness of contaminant mitigation devices. Studies have been directed toward defining the potential impact of contaminant containing stormwater on receiving water bodies. Contaminants of concern in highway runoff include metals, organics, and suspended solids. Although several management practices have been utilized, their implementation can be prohibitively expensive and logistically challenging. The logistical challenges result from space limitations and, more significantly, from the sheer magnitude of areas generating runoff and the volume of runoff generated. These difficulties preclude the implementation of best management practices at all locations. Consequently, it would be desirable to understand the contaminant removal potential of existing highway appurtenances and develop information that could be used to define their removal potential under differing system conditions. One such appurtenance is the highway grass strip; a grass strip associated with the highway shoulder.

To determine the effectiveness of these grass strips as a retention mechanism, a full-scale grass strip model was constructed that allowed control of slope and stormwater contaminant feed rate. The model was 1.2 m wide (perpendicular to flow path) and contained a 3 m grass section. A simulated highway stormwater was developed that contained sediment, lead, cadmium, copper, and zinc. The research approach was divided into three main areas: (i) determination of the hydraulic retention time for various slope and flow combinations, (ii) estimation of retention times for selected metals, (iii) analysis of the fate of the metal contaminants with regard to spatial location as well as plant uptake. Hydraulic detention time over a range of slope/flow combinations was estimated using a bromide tracer technique. Contaminant fate and retention was estimated by applying stormwater at a fixed slope and flow during nine simulated storm events. In addition,

standard metal partitioning information was collected by developing adsorption isotherms for each metal on the stormwater sediment and grass strip soil.

Hydraulic retention times (HRT) ranged from 8.8 minutes at a flow of 3.8 L/min•m and slope of 17%, to 85.3 minutes for a flow - slope combination of 0.38 L/min•m and 5%. The data indicated that an equivalent percent change in flow had a greater affect on HRT than slope. Metal partition information and the Ogata-Banks solution to a one dimensional advection-dispersion equation were used to calculate theoretical metal retardation times, which ranged between 183 days for lead and 30 days for copper. These predictive estimates could not be confirmed with the data collected since no significant metal breakthrough was observed in the grass strip over the duration of experimentation.

The largest portion of metals were retained within the initial 1 m of the grass strip and 1.0 cm of depth. These analytical findings were supported by visual observations that indicated that the stormwater sediment was retained in the upper 1 m of the grass strip. Overall metal retention was estimated by mass balance and it was determined that 84% of zinc, 93% of lead, and >99% of cadmium and copper applied to the grass strip was retained.

Clover predominated the site during the simulated stormwater period of experimentation and its general health was observed to deteriorate throughout these experiments. The vegetation appeared to be metal excludor species as the dry weight concentration of metals contained in the vegetation was less than the dry weight soil concentration.

Based on the data collected in this study, grass strips along highway shoulders can retain significant sediment and metal concentrations. Future work should include a long term study at a field site to better assess the impact of time on retention efficiency.

INTRODUCTION

The Problem

The Washington State Department of Transportation (WSDOT) is sensitive to the effect contaminants found in highway runoff have on receiving waters within the state. Many national monitoring tests have been conducted to determine the concentrations and sources of highway stormwater contaminants. In conjunction to the monitoring tests, the listing of priority pollutants in the 1977 Clean Water Act included heavy metals such as lead, cadmium, copper, and zinc, all of which can be found in highway stormwater. The 1987 amendments to the Clean Water Act and the Puget Sound Water Quality Management Plan increased regulation to specifically include highway stormwater runoff. Thus, WSDOT has focused its attention on determining possible methods to reduce highway contaminant transport to surface waters. Present conventional treatment mechanisms, such as detention basins, grassy swales, infiltration galleries, and vegetated filter strips, were the first mechanisms examined for potential contaminant removal. However, all of the aforesaid methods are limited by the volume of runoff that they can treat effectively. There are many miles of highway in Washington, and the total volume of highway stormwater runoff produced in a single storm event would require a significant number of detention ponds, infiltration galleries, as well as vegetated swales and slopes.

A truly effective retention mechanism for the treatment of highway runoff would be able to retard or remove contaminants as they came directly off the roadway. It has been found that vegetated shoulders and slopes can retain sediment and metals from highway runoff (Bell and Wanielista, 1979; Wigington *et al.*, 1986; Lagerwerff and Specht, 1970; Motto *et al.*, 1970; Gish and Christensen, 1973). Therefore, it may be possible that highway grass strips can be designed as a removal mechanism for runoff contaminants. These grass strips, or shoulders, could provide a low maintenance treatment method for the retention of highway runoff contaminants.

RESEARCH OBJECTIVES

The overall objective for this research was to determine the effectiveness of highway grass strips as a possible non-point source retention mechanism for heavy metals. The research was divided into three main tasks. The first task was the design and construction of a full-scale test plot of a highway grass strip. The laboratory test plot allowed for the variations of both slope and flow which are the main design parameters of a grass strip, without the effects of variations in the soil type, vegetation, and moisture conditions which would be present in a comparison of various field grass strips. The second task was the determination of the hydraulic characteristics of the test plot by both visual observations and the estimation of the hydraulic retention times for various combinations of slope and flow. The third task was estimating the theoretical retention times for each of the four metals studied, by calculating the retardation factors using single-solute isotherm data. Once these tasks were completed, metal migration experiments were conducted to estimate the actual migration of the metals through the test plot for a single slope/flow combination. Soil cores were taken after the migration studies were completed to locate the position of the retained metals. The vegetation was also monitored throughout the migration study for its metal uptake ability.

REVIEW OF PREVIOUS WORK

Constituents of Highway Runoff

Many researchers have tested and studied the pollutants found in highway runoff. Field (1993) compiled typical concentrations of highway runoff pollutants from different locations such as, Northhampton, England; Durham, North Carolina; and Syracuse, New York. Barrett *et al.*, (1993) also compiled an extensive literature review listing measured average ranges for many known highway contaminants given in Table 1.A (Appendix A).

Selected contaminants have been listed in Table 1. Driscoll *et al.*, (1990) determined pollutant concentrations segregated by highway type and geographic location. The information provided was a direct result the National Urban Runoff Project (NURP). An outline of his findings are given in Table 2.A (see Appendix A). These data indicate a high degree of constituent type and concentration variability. This variability and the intermittent nature of the storm events are some of the greatest challenges with respect to treatment.

Table 1. Range of average values for stormwater contaminant concentrations for selected highway contaminants (Barrett *et al.*, 1993).

Contaminant	Concentration (mg/L)	Load (kg/ha/year)	Load (kg/ha/event)
Suspended Solids -	45 - 798	314 - 11,862	84 - 107.6
Lead	0.073 - 1.78	0.08 - 21.2	0.008 - 0.22
Phosphorous, as P	0.113 - 0.998	0.6 - 8.23	
BOD ₅	12.7 - 37	30.6 - 164	0.98
Polyaromatic Hydrocarbons		0.005 - 0.018	

Present Treatment Mechanisms for Highway Runoff

Until recently, stormwater control systems have been designed solely on hydraulic considerations, such as retention times and applied flow rates. Thus, the removal of pollutants was a consequential occurrence. The first options examined for possible contaminant removal were the hydraulic controls presently in use at many locations. All of these treatment mechanisms were effective but limited by the amount of runoff volume they could treat.

Detention Basins

Detention/retention basins are man-made catchments designed to control excess runoff from a storm event. Three types of detention basins are:

- Dry ponds, holding storm overflow for a short amount of time.
- Extended dry ponds, similar to dry pond with a longer holding time.
- Wet ponds, designed for a continual low level of water.

Dry ponds are the least effective at 0 to 20 % removal for most pollutants. Extended dry ponds have 40 to 70 % removal for particulate contaminants, but much less for dissolved types such as soluble BOD. Wet ponds, if maintained properly have been rated at 50% to greater than 90% for SS removal, 40 to 60 % for nutrient removal, and 40 to 45 % for zinc (Zn) (Yu and Nawang, 1993). Two studies (Cole, 1993 and Price, 1994) were conducted on a model of a detention basin near Olympia, Washington. Cole determined that the metals Pb, cadmium (Cd), copper (Cu), and Zn were decreased by 34 to 40 % depending on the metal and the flow applied. Price supported Cole's findings by showing that the addition of a coagulant and an added baffle increased removal by up to 80%. Two potential disadvantages of detention basins are their limited capacity and the build-up of sediment to the point where the basin must be dredged. The accumulation of contaminants, such as heavy metals, in the sediment may complicate the disposal of the dredged sediment.

Infiltration Facilities

Infiltration systems are detention basins with a permeable bottom. They are designed to remove contaminants while allowing the water to enter the groundwater system (WSDOT 1995). As pollutants accumulate in the infiltration section of a basin, these pollutants may be transported into the groundwater over time if the filter material capacity is exhausted prior to replacement. In the case of metals and other adsorptive pollutants, the possibility exists that organic compounds, such as humic and fulvic acids, may affect their solubility and adsorptive capacity. Thus, depending on the organic ligands present and the soil type, the metals could remain in solution and reach the water table much quicker than expected or be retained at a higher rate than if no organics were present (Jordan, 1995 ; Igloria, 1995).

Grassy Swales

Swales are trenches located along highways, such as the median of major interstate freeways. Swales were the first type continuous flow removal mechanism studied that treated large volumes of runoff from large sections of highways. Yousef *et al.* (Best

Management Practices, 1985) determined that pollutants can be retained in a swale by adsorption, precipitation, and/or biological uptake. He also discovered better removal with a newly constructed swale prior to the establishment of vegetation. His conclusion was that soluble metals are mainly removed by adsorption due to the soils adsorptive capacity. Plant material growing in the swale, decreased the contact area between the metals and the soil, thus reducing the actual number of adsorptive sites. In contrast, a study completed by Bell and Wanielista (1979) determined that an increased concentration of organic material (mainly humic substances) and vegetation increased the removal of metals from runoff. Therefore, the presence or decaying plant material in a swale may increase the removal potential of a swale by the addition of a greater number of adsorption sites for the metal.

Current design criteria of a biofiltration swale as a best management practice (BMP) have been outlined by WSDOT in the *Highway Runoff Manual* (Feb. 1995). Design is based on the shape, size, and expected flow as follows: length of 61 m, maximum width of 3 m, and maximum 10 cm depth under 6-month storm condition. Vegetation should be fine, close-growing and water-resistant grasses. General maintenance (including mowing, sediment removal, periodic inspection, and liter removal) of the swale is required to insure the continuing effectiveness of the vegetation as a filtering mechanism. Based on the limiting depth of flow criteria set forth by WSDOT, not all of the potential highway runoff can be treated by a grassy swale.

Vegetated Filter Strips

A vegetated filter strip could be considered any sloped section of grassed or forested ground that can provide stormwater treatment of pollutants. They differ from the grassy swales in that the applied flow is generally less than the flow in a swale. The depths of flow do not generally top the vegetation in the biofilter.

WSDOT has specified the use of vegetative filter strips for use as a BMP for rural highways (Average Daily Traffic, ADT, less than 30,000, WSDOT 1995). The runoff

must not be from more than two lanes of traffic and be applied to the shoulder as sheet flow. Criteria for the use of a vegetated filter strip as BMP are:

- The filter strip must be at least 3 m in width (distance perpendicular to the roadway) with a transverse slope no greater than 15 percent
- The longitudinal slope of the roadway must not be more than 5% due to the difficulty in maintaining a sheet type flow.
- After treatment, the stormwater must be conveyed to a stormwater quantity BMP.

Vegetated filter strips are usually a preliminary treatment for an infiltration gallery, detention basin, or other water quantity BMP. Albrecht and Barfield (1982) have determined that vegetated filter strips can have effective removals of fine sediment of up to 99%. Dillaha *et al.*, 1986 determined that the most significant factor affecting the removal efficiencies was the flow regime. Flow pathways for highway runoff are surface channels and pools, seepage through a shallow ‘muck’ layer (Kadlec, 1990), or transport through the soil. The significance of each mechanism will depend on the soil moisture content, the grass type and density, the roughness, slope, etc.

Highway Shoulders and Grass strips

Based on the definition of a vegetative filter strip, highway shoulders and grass strips can be considered rudimentary filter strips. Grass strips are designed for the safety of motorists with the degree of slope ranging from 5% to 25% depending on the location of the roadway. Their width is mostly grassed averaging around 3 m down gradient of a paved or graveled region that is directly adjacent to the roadway. Areas in which a grass strip can differ from vegetated filter strips are in the application of flow and their roadway ADT. The runoff can come directly from the roadway, or a higher volume of runoff may have channeled to a common discharge location. From design storm hydrographs for the Olympia/Seattle area, the runoff is generally less than 8 L/min assuming all runoff flows

directly from the highway to the shoulder and using a type IA storm event, 40.5 m² total runoff area, and a 4 lane highway (WSDOT 1994).

Highway shoulders may be of greater slopes than specified for a grass strip. In these cases, contaminants may still be retained in the soils of the shoulder. Though, the retention capability at these higher slopes is expected to decrease. WSDOT is currently conducting studies, such as this one, to determine if design criteria presently used for vegetative filter strips and criteria for grass strips may be combined to incorporate a broader application of highway runoff treatment.

Operation and Retention Mechanisms of a Highway Grass strip

Flow Paths Through a Grass strip

As the water travels down the grass strip the flow regime changes dramatically and is dependent on the antecedent moisture, grass density, and soil type. Three possible flow paths are present and will occur simultaneously at varying degrees. They are movement through the soil layer acting as a true groundwater flow, overland flow, or flow through a shallow surface ‘muck’ layer as defined by Kadlec (1990). Overland flow is expected to have the most impact on decreasing the retention times of metals in a grass strip and occurs mainly under two conditions, a low permeability soil, such as a hard-packed clay, or highly saturated soils. Stout (1995) classified five sequential steps in the shallow overland flow encountered by a grass strip: (i) the surface becomes completely saturated, (ii) depressions are filled, (iii) concentrated flow initiates through preexisting flow paths, (iv) these small flow paths converge forming shallow sheet flow, and (v) as the storm event decreases sheet flow reduces and a reversal in the sequential steps is realized.

Runoff events following an extensive dry period are considered to have the highest concentrations of pollutants due to a large amount of sediment and contaminants to be deposited on the roadway. Therefore, the flow regime under these conditions may be predominantly within the root zone due to the unsaturated condition of the soil. A greater amount of filtration and partitioning will occur in the root zone, increasing the retention

potential of the grass strip until the slope becomes saturated and overland sheet flow occurs.

Heavy Metal Retention and Migration

Highway shoulders have been shown to contain metals from highway runoff (Hewitt and Rashed, 1992 ; Bell and Wanielista, 1979). Metals are deposited along the highway shoulder either by wind-blown dust particles or by stormwater washing the highway surface. Once onto the grass strip, metals can be retained by filtration (Maestri *et al.*, 1988), partitioning onto the soils and grasses (Motto *et al.*, 1970 ; Wigington, 1986), be taken up by the biota in the grass strip, whether plant or animal (Fergusson, 1990 ; Motto *et al.*, 1970), or migrate through the soil with the infiltrating runoff (Wang *et al.*, 1980 ; Bell and Wanielista, 1979). Subsequent storm events have the potential to move the pre-existing metals down gradient, as well as adding more metals to the grass strip. In the field, all these possible pathways of metal transport or retention exist, but are very difficult to define. In addition, the metal previously applied to the grass strip can affect the local equilibrium within the grass strip and thus the performance of the entire system. Eventually a 'steady-state' is expected to exist so that the concentration of metals entering the grass strip would be equivalent to the exit concentration.

Metal species found in highway runoff are mainly partitioned onto small particulate matter (Cole, 1993). During a runoff event, the metals are exposed to continually changing conditions and very complex local equilibrium conditions. The metal can remain partitioned to the particulate roadway dust, enter the aqueous phase, partition onto the soil of the grass strip, become complexed to organic material in the soil either aqueous or solid phase, adsorb to the biota of the grass strip, or be absorbed into the biota. Any movement of the metal species, change in concentrations, introduction of a different metal species, or the presence of organic matter alters the local equilibrium conditions and thus the state and mobility of the metal. It is assumed that any one or combination of these conditions occur

numerous of times during a runoff event, depending on flow intensity, soil types, metal species, organic content, grass density, and previous metal concentration.

Lateral Movement of Heavy Metals

Studies have been completed on the movement of metals along grass-lined channels and swales (Yousef *et al.*, Best Management Practices, 1985 ; Wanielista *et al.*, 1985 ; and Wang *et al.*, 1980), but examination into the migration through the preceding grass strips and shoulders have not been completed. It is important to understand how the metals are migrating within the shorter widths of grass strips and shoulders to be able to determine their application as retention mechanisms.

The numerous complex interactions between metals and grass strips add to the difficulty in understanding their effectiveness in retaining highway pollutants. Even so, many studies have shown that the vegetated areas, mainly grassed swales, adjacent to a highway are effective in the retention and possible removal of highway contaminants. In a sampling study, Lagerwerff and Specht (1970) determined that metal concentrations in roadside soils decreased consistently for all metals tested at 8, 16, and 32 m from the roadway, with the following order from greatest concentration to the least, Cd>Pb>Zn>Ni. Gish and Christensen (1973) determined similar results over a distance of 50 m from the roadway. A highway grass strip is stated to average 3 to 4 m in width from the roadway (WSDOT 1994). The concentrations determined by Gish and Christensen (1973) were, on average, 50% greater within the grass strip width than at any greater distance from the roadway. Lateral movement of metals is an apparent phenomenon in vegetated areas adjacent to highways, but to what extent the movement occurs in a grass strip and if a 'steady-state' condition is reached remains undetermined.

Vertical Migration of Metals

In constructing grass strips, the subsoil has been compacted to limit the amount of erosion and supply the necessary structural integrity of the roadway. The hard-packed layer of soil can enhance the movement of the infiltrated runoff in the direction of the slope

versus a complete vertical movement toward the water table. Metals can migrate vertically with the infiltration and will partition to the soil matrix as the stormwater infiltrates deeper into the grass strip. Metals will thus have a vertical concentration gradient, as well as one which is a function of length.

Vertical metal migration has been discovered to be limited to within the first foot of depth, depending on the metal and soil type. Laxen and Harrison (1977) stated that Pb is generally retained within the top 15 cm of soil. Whereas, Cd usually has a less distinct concentration gradient even beyond 15 cm of depth (Wang *et al.*, 1980). Lagerwerff and Specht (1970) and Motto *et al.*, (1970) also completed vertical migration studies concluding that Pb has a rapidly decreasing concentration gradient with increasing depth. Lagerwerff and Specht (1970) also examined soil cores for Zn, Ni, and Cd, discovering that these metals also decreased in concentration with increased depth. Zinc maintained a gradient similar to Pb, while the Cd gradient was much less pronounced. These sampling studies were completed over 30 to 50 m distances from the roadway. This distance included both a highway grass strip and a grassed swale. Therefore, their conclusions may not accurately represent the vertical gradients within initial 3 m highway grass strip adjacent to the source of the metal-laden runoff.

Plant Uptake of Metals

Plants rely on the soil to supply nutrients for survival. Metals found in the soil have the potential to be adsorbed into and onto plant material. Some metals are considered micronutrients (Zn and Cu) with fairly high phytotoxic levels. Whereas, other metals have no biological significance and low phytotoxic levels (Pb and Cd). The excess, or unnecessary metals, once adsorbed, are stored in various parts of the plant depending on metal and plant species. For example, cadmium is generally found in the leaves. However, lead has been found to remain primarily in the root zone. (Fergusson, 1990)

Plants have been divided into three categories, as far as metal uptake and the toxic effects of the metals on the plant are concerned: (i) accumulators, (ii) indicators, and (iii)

excludors (Davis, 1992). Accumulators are those plants that will concentrate metals in their tissues, regardless of the soil concentration. Indicators will maintain a closely correlated concentration of metals in their tissue with the concentration in the soil. Excludors will only contain a low concentration of metal in their tissue due to a natural enzymatic exclusion mechanism at the soil-root interface. The exclusion will occur until the restrictive mechanism breaks down, a phenomenon that occurs above a certain concentration (Davis, 1992). Chamberlain (1983) studied lead uptake in plants and developed a concentration factor (CF) to help classify plant metal uptake, which is the ratio of the metal concentration in dry weight of plant material to the total metal concentration in the dry weight of soil.

Highway shoulders are presently planted with native grass species that require low maintenance, are hearty, and maintain a good root system to limit erosion. Past studies in plant uptake of metals have generally been concerned with the introduction of metals into the food chain. There is little, if any, information about the uptake abilities of the grasses used for highway cover. The WSDOT seed mix for western Washington includes perennial rye grass, red fescue, colonial bent grass, and white Dutch clover (Table 3.A, Appendix A). Jones *et al.*, (1973) studied perennial rye grass in 16 different soils, all with an average soil solid phase Pb concentrations of 50 mg/g dry weight. He determined that the lead in the plants poorly correlated to that in either the total or extractable lead in the soils.

The grasses of a grass strip have the potential to be a significant sink for metals which could easily be removed by harvesting the clippings. Many different species have been determine to hyperaccumulate metals especially zinc, such as *Thlaspi caerulescens*, *Alyssum tenium* and *A. lesbiacum* (McGrath *et al.*, 1993). Most hyperaccumulators are selective as to which type of metal that they will accumulate. No such study was found for the vegetation of the WSDOT seed mix specified. Therefore, the metal uptake of the grasses was monitored to determine their metal uptake.

RESEARCH APPROACH AND PROCEDURES

Model Design and Construction

There are many factors that affect the ability of a grass strip to retain metals from highway runoff, such as antecedent moisture conditions, soil type, organic content, and flow rate. A full-scale model of a highway grass strip was designed and constructed that allowed the slope and flow to be varied without the effects of significant variations in other factors. The model consists of three main structures: the test plot, the flow introduction system, and the sampling structures.

Test Plot Design

The test plot (Figure 1) outer frame had the basic dimensions of 4.27 x 1.22 x 0.46 m (width x length x depth). The frame was constructed of 10.16 cm angle iron. The interior framing was wood with the internal dimensions of 4.11 x 0.99 x 0.38 m. The test plot was designed to be capable of rotating from a 0 % to a 50% slope. Rotation was afforded by a triangular pivot placed 2.21 m from the down gradient end of the plot. A chain hoist was used to raise and lower the test plot to the selected slope. Local Palouse topsoil, obtained from a nursery, was used to fill the plot. The vegetation planted was a WSDOT seed mix for the Olympia/Seattle area (see Appendix A). Gravel was placed in the first 1.22 m of the box to a depth of 15.24 cm. Gravel size, placement, and soil compaction levels were based on the specifications listed in the *1991 Standard Specifications for Road, Bridge, and Municipal Construction* (WSDOT 1991).

A double-liner system was incorporated into the test plot design, to eliminate the possibility of water flowing along the bottom due to a smooth interface between the test plot soil and liner. The primary liner was a bentonite geotextile, increasing roughness between the bottom of the soil and liner. The geotextile was donated by Gundle Lining Systems, Inc. of Houston, Texas and consisted of a 0.64 cm bentonite layer adhered to 20 mm PVC sheeting. To prevent sub-surface channeling, a 1.28 cm layer of granular bentonite was placed between the test plot soil and liner. A shallow soil layer was placed

between the primary liner and the internal wood framing and was formed to make a trapezoidal channel to decrease wall effects. A 20 mm PVC liner was the secondary liner to protect the internal wood framing. A schematic of the test plot cross-section showing the double liner system is given in Figure 2.

Sampling Structures

The sampling structures consisted of a sub-surface sampling well and a surface sampling cup at 15 locations throughout the test plot. The well-cup structures were located at 0.61 m intervals along the width of the test plot. Each 0.61 m interval consisted of a set of three wells and associated surface sampling cups. A matrix of the sampling locations is illustrated in Figure 3. The sub-surface sampling wells were constructed of 1.28 cm PVC piping in 0.31 m lengths with perforations over the bottom 20.32 cm. Preliminary testing indicated no detectable metal partitioning to the PVC. A 70 μm Teflon mesh was used to keep fine particles from entering the sample wells.

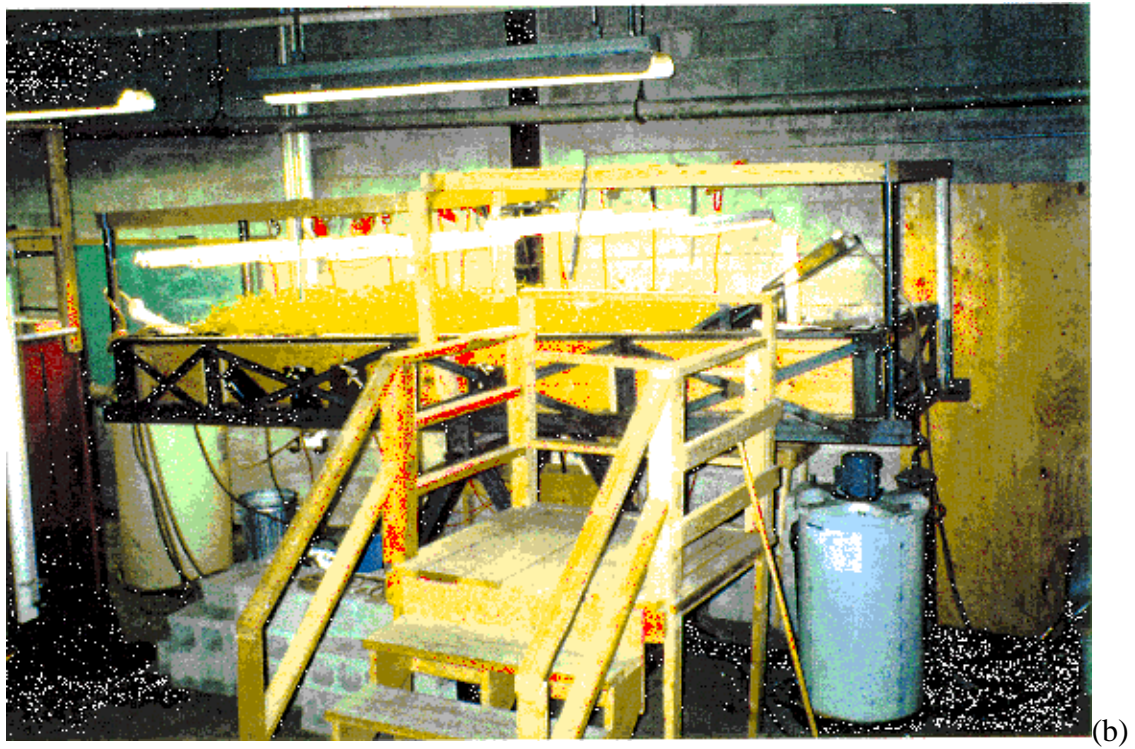
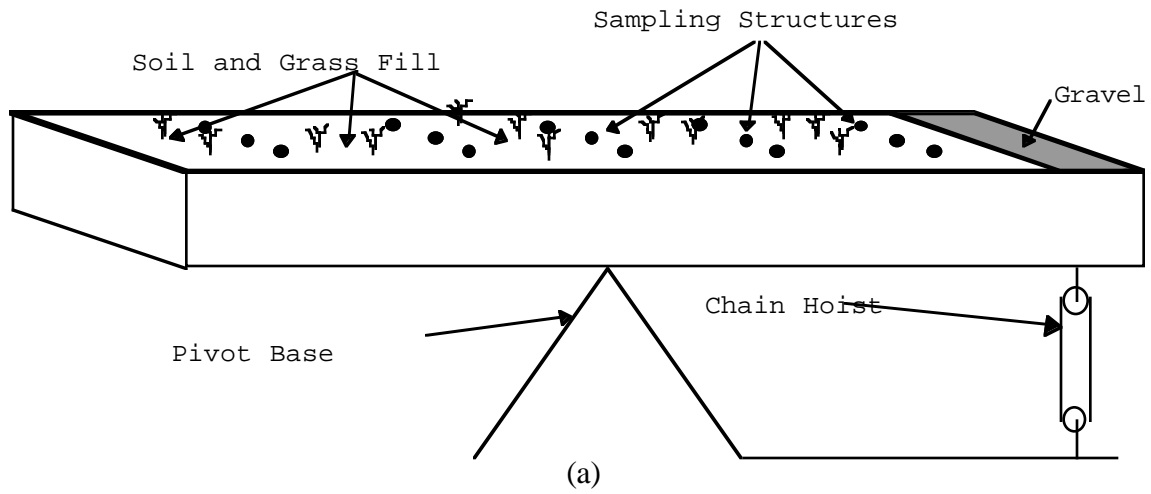


Figure 1. The experimental test plot. (a) schematic, (b) actual test plot.

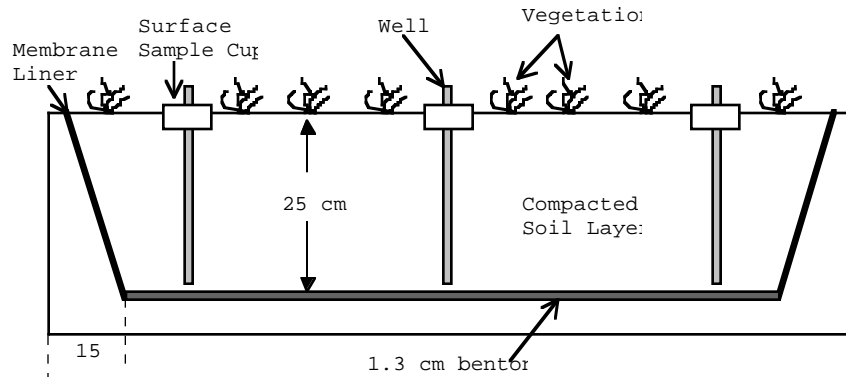


Figure 2. Cross-section of the test plot with well-cup sampling structures.

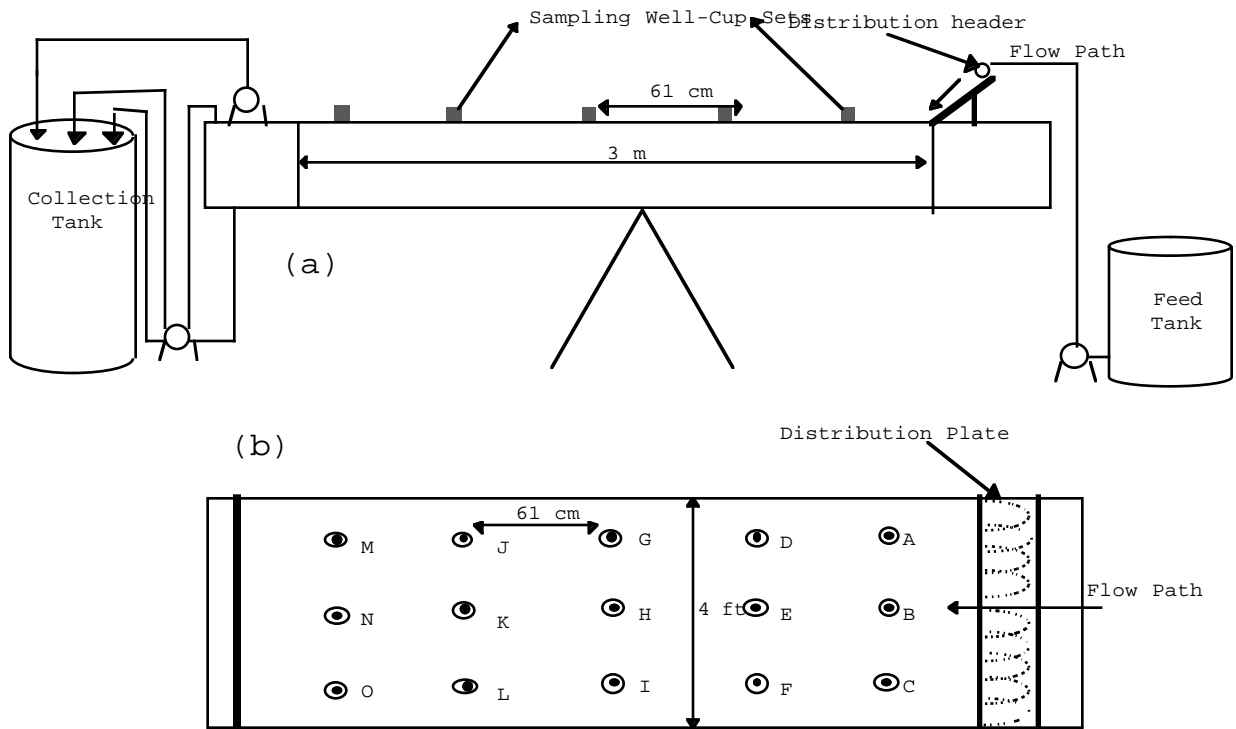


Figure 3. A schematic representation of the sampling structure matrix. (a) side view, (b) top view.

The surface sample cups were made from Nalgene bottles with a 1.28 cm front facing the flow and a 5.08 cm back to catch runoff entering the cup. A notch was made in

the cup to allow for slightly subsurface flow and low flows from the front of the cup to be collected. The cups were placed at the top of each sample well to prevent surface water from flowing down the well casing and interfering with subsurface sample collection. The sampling structures are detailed in Figure 4. To insure a separation of surface and subsurface flows, the soil directly beneath the sample cups was packed tighter than the surrounding soil, and a silicone sealant placed between the wells and the cups. Bromide tracer experiments were used to assess the integrity of the well-cup sampling structures.

The outlet of the test plot was constructed of a slotted 10 cm PVC piping wrapped in a fiberglass screen to exclude large particles. During experimentation, some of the flow seeped to the surface at the down gradient end of the test plot and was removed by pumping from a small depression into the discharge collection tank, 416 liter Nalgene reservoir (Figure 3).

Flow Introduction System

The flow introduction system was designed to produce an even distribution of flow across the width of the test plot. The flow header was a 0.64 cm PVC slotted pipe that extended the 0.99 m length of the test plot. The header was located on a flow distribution plate set at a 30° angle where water was forced into the necessary sheet pattern (see Figures 2b and 3). The flow plate was placed 3 m up gradient of the final sampling set. The feed tank was a completely mixed 208.2 liter Nalgene reservoir pumped directly into the header using a variable speed peristaltic pump (Figure 3).

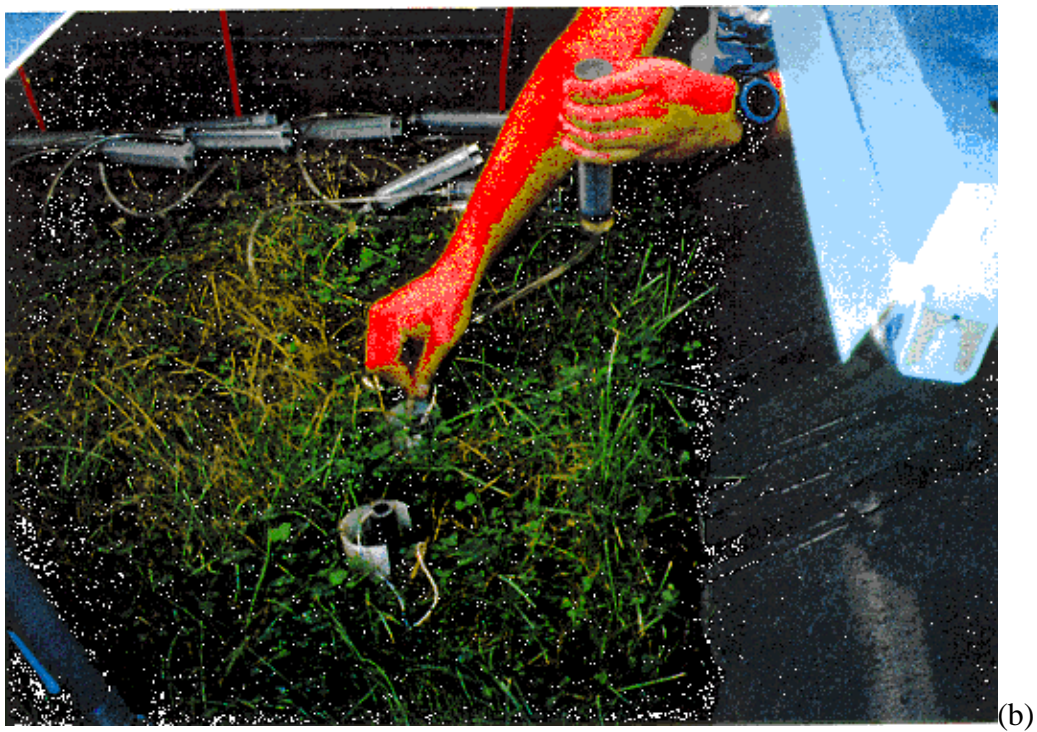
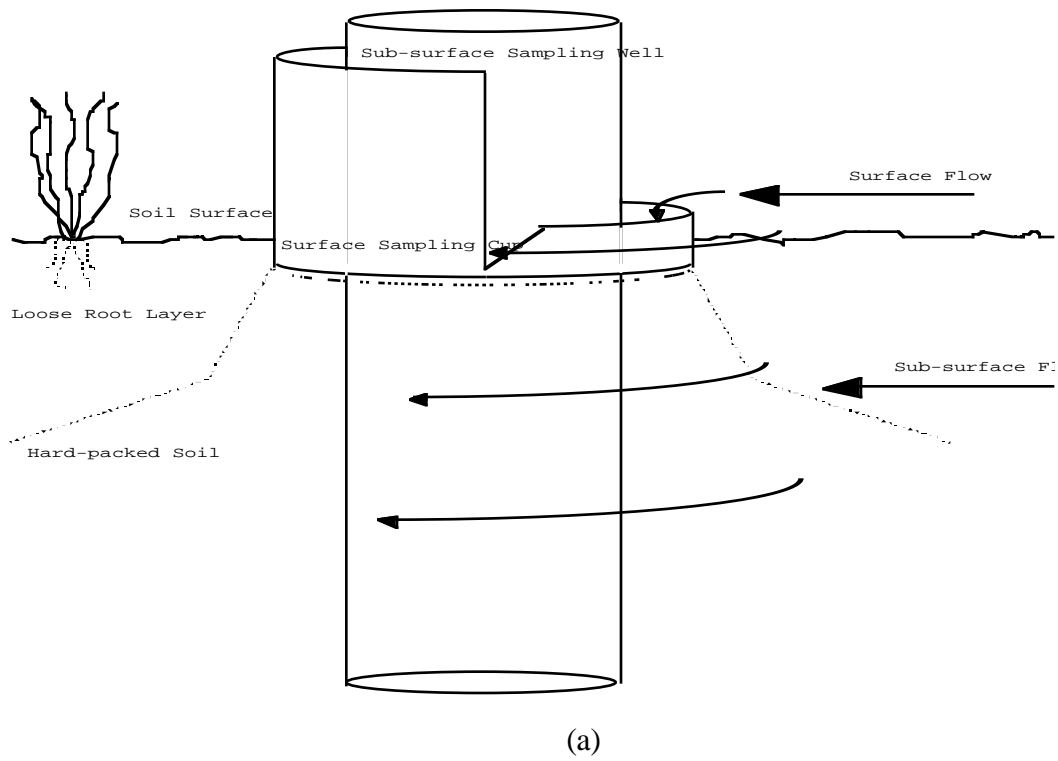


Figure 4. Sampling structures (a) schematic and flow patterns (b) sample cups in the test plot

Experimental Design

Grass strip experimentation was divided into five major areas: (i) storm flow and contaminant selection, (ii) characterization of the test plot soil, (iii) hydraulic characterization of the test plot, (iv) metal migration estimation and testing, and (v) determination of metal sinks.

Storm Flow and Contaminant Selection

Six design storm hydrographs, presently used for the design of highway drainage systems, (Appendix C) were supplied by WSDOT for the Olympia/Seattle area. Each hydrograph was calibrated for three different roadways, a 4-lane, a 2-lane, and a single lane road. The storms were of type IA, typical of western Washington, with a total rainfall depth of 4.55 cm. The peak runoff ranged from 7.8 L/min to 1.5 L/min for a runoff area of 40.5 m².

Each experimental run consisted of (i) initial saturation, (ii) a first-flush, and (iii) a wash-out or flushing section. First flush was used to describe the phenomenon where a large portion of the pollutant load is being contained in the initial portion of the runoff event (Hewitt and Rashed, 1992). The first-flush section is based on 80% of the contaminant being found in the initial 20% of the runoff volume (Bellinger *et al.*, 1982). The wash-out section was selected as one-half of the remaining runoff volume. It contains the high flows associated with the peak rainfall intensity. The higher flows could force pollutants down the grass strip.

Therefore, the selection of these four metals was based on past knowledge of adsorption characteristics and knowledge of their presence in highway runoff. Eight stations from the national monitoring study completed by Driscoll *et al.*, (1990), two of which were located on I-5 and State Route 520 near Seattle, were used to define the metal concentration to be applied to the test plot. The average concentrations for these sites are listed in Table 2.A, Appendix A. These values were also supported by a literature review

published by the Center for Research in Water Resources, University of Texas, Austin (Barrett *et al.*, 1993), including many geographically specific tests of highway runoff. Simulated stormwater was created to mimic western Washington concentrations of total suspended solids (TSS), Pb, Cd, Cu, and Zn based on these studies (Table 2).

Table 2. Simulated stormwater mix applied to the test plot.

Contaminant	Concentration (mg/L)
Suspended Solids	250
Lead	2.425
Cadmium	0.075
Copper	0.199
Zinc	2.055

Soil from an alluvial fan in Wallowa Lake, Oregon was used for the suspended solids in the simulated stormwater. This sediment from the beach of Wallowa Lake was determined to be free from any major anthropogenic sources of metals, such as mining or highway runoff (Cole, 1993). Those particles which passed a 200 mesh sieve ($< 75 \mu\text{m}$) were used in the experimentation.

Characterization of the Test Plot Soil

As mentioned, the soil used to fill the test plot was a local Palouse top soil with a similar clay fraction, though different clay type than western Washington. Particle size distribution tests were completed by both sieve and hydrometer analysis (see Appendix B). Using a 1N HNO₃ digestion, background concentrations of easily extractable metal were determined for the four metals in question. Additional background tests were conducted on the test plot soil by the Analytical Sciences Laboratory, Moscow, ID. The soil was examined for organic matter, organic carbon, and cation exchange capacity (CEC) to get an estimate of the potential of the soil's ability to partition metals. Table 3 describes the test plot soil referencing its adsorption potential, size distribution, and background concentration of metals.

Table 3. Background characterization of the test plot soil.

Background Parameters	Result	Units
% finer than 75 μm	21	%
% finer than 10 μm	5	%
Lead, Pb	0.0509	mg/g
Cadmium, Cd	0.0009	mg/g
Copper, Cu	0.0690	mg/g
Zinc, Zn	0.1018	mg/g
CEC	33.1	cmol(+)/kg
% organic carbon	8.7	%
% organic matter	14.98	%

Hydraulic Characterization of the Test Plot

To understand the effect of slope and flow on grass strip retention of metals, various combinations of slope and flow were tested and their hydraulic characteristics determined by performing bromide tracer experiments. The combinations represent extremes of expected field combinations. The range of flow was determined using the method described in Storm Event Simulation, and was found to 0.38 L/min-m to 1.9 L/min-m. WSDOT lists highway runoff as flow per unit length of roadway, which will be followed throughout the remainder of this report. The grass strip slope design criteria ranged from 5 to 25%. Combinations of the extreme values were tested and are listed in Table 4. Run #9 was a requirement placed on WSDOT by the Washington State Department of Ecology (WADOE) to allow grass strips to be considered a potential contaminant retention mechanism.

Table 4. Experimental Combinations of Slope and Flow.

Run #	Flow (L/min-m)	Slope (%)
4	0.38	5
5	1.9	5
6	0.38	25
7	1.9	25
8	0.38	5
9	3.82	17

Bromide was used as a non-reactive conservative tracer to determine the hydraulic retention time (HRT) of the test plot under each experimental condition. Prior to the application of the tracer, a 208.2 liter saturation tank of water was applied to the test plot. This application served two purposes. One, it was assumed to saturate all preferential pathways of flow through the test plot. The second is that any residual bromide from the previous run that had diffused into the sample wells or the preferential pathways would be washed through the test plot. At the end of saturation application, each well was sampled, as well as any surface cup that contained water. This sample set was reported as $t = 0$.

Immediately following the completion of the saturation tank, a bromide tracer solution was applied to the test plot at a concentration of 50 mg/L. The tracer was applied as a step input lasting approximately 3 hours for each storm type to simulate the first-flush phenomenon. After the first-flush volume was applied, tap water with no tracer was applied to the test plot to simulate the wash-out portion of the hydrograph. In the initial tracer runs, the tracer would reach approximately 7% of the feed concentration after 300 to 350 minutes of wash application with minimal decrease in concentration thereafter. Thus, the flushing section of the run was ended after 350 minutes.

Samples were taken at predetermined time intervals depending on the experimental conditions. Samples were taken in each well and at the surface sites which contained water. Each sample was diluted by a ratio of 1:10, then filtered through a 0.45 μm filter. The filtered samples were analyzed for bromide using a Dionex 4000i series ion chromatograph equipped with an AS-12 column and a carbonate isocratic eluent configuration.

Metal Migration Studies

Single-solute adsorption partition coefficients were determined for the test plot soil to determine a retardation factor for each metal to calculate a theoretical metal retention time

(MRT). Metal migration experiments were conducted to estimate actual retention times for comparative purposes.

Adsorption Isotherm Procedure

Singe solute adsorption isotherms were developed using the procedure outlined in Appendix D. For Pb, Cu, and Zn, the range of initial liquid phase concentrations which produced a linear isotherm was determined to be 75 mg/L to 25 mg/L. Whereas, the range for Cd was 45 mg/L to 2.5 mg/L. These concentration ranges were applied to both the Wallowa Lake sediment and the test plot soil. A constant soil mass of 5 g was used for all test plot soil isotherms and for the Cu and Cd Wallowa Lake sediment. Due to the high degree of adsorption of both Pb and Zn to the Wallowa Lake sediment, only 1 gram of soil was used to produce a linear isotherm at the same initial concentrations.

In an attempt to define the state of the metals in the feed solution, a competitive adsorption test was completed at the sediment and metal concentrations used for the simulated stormwater feed solution (see Table 2). Three replicate reactor bottles were tested. To determine adsorption to the bottle and background concentrations, a metal blank and sediment blank were also tested. Each reactor bottle was allowed to reach equilibrium by shaking for 24 hours and the liquid phase, following filtration, the liquid phase equilibrium concentrations were measured by atomic adsorption spectroscopy. The solid phase equilibrium concentration was then calculated using a mass balance approach.

Metal Migration Experiments

Metal migration experiments were conducted to determine the accuracy of the isotherm estimation and the actual migration of the metals through the test plot. A large factor to account for in the test plot, as well as in the field, is the accumulation of metals or the 'history' of storm events. To account for the history of storm events, identical successive runs were completed to limit the effects of flow and slope variations altering the retention time. The experimental conditions selected were that of tracer run #7 with a 1.9 L/min-m flow and 25% slope. The selection was based on the shortest HRT which was

expected to result in the most expedient metal breakthrough. The conditions imposed on WSDOT by WADOE ,though higher, were not selected due to the flow being a peak flow applied for a much longer time than expected in the field.

A total of 6 experimental runs were completed. Each run was approximately 230 minutes in length with approximately one week between runs. An experimental run was considered to represent a single storm event. The time for breakthrough was, therefore, based on total elapsed storm time, disregarding the time between experiments in which no run was being conducted. The preliminary saturation volume applied prior to each run was also not considered in the determination of the elapsed storm time. The elapsed storm time for the migration study totaled approximately 23 hours of simulated storm events over the six experimental runs.

Metal migration experiments were conducted in the same manner as the tracer experiments. A saturation tank of 208.2 liters was applied prior to the actual simulated stormwater feed. At the end of the saturation tank, samples were taken and recorded at time, $t=0$. The simulated stormwater was mixed and immediately applied to the test plot. The feed tank was constantly mixed to maintain feed solution homogeneity. No flush volume was applied after the simulated stormwater to eliminate any enhanced migration of the metals due the rapid change in the equilibrium conditions with the application of tap water.

Samples were taken at regular intervals from both the wells and the producing surface cups. The interstitial wells were considered to be of lesser importance than the final set of wells (MNO) and the discharge of the test plot. Therefore, samples were taken less frequently, and were used to track the metal migration as a function of total elapsed storm time. The sampling intervals are given in Table 5. The feed tank was sampled on three occasions during each run to determine if vertical concentration gradients occurred and to determine an average concentration for the entire run.

All samples were then analyzed for Pb, Cd, Cu, and Zn. In analyzing for metals, it was necessary to acidify liquid samples to insure a limited amount of adsorption to sample containers.

Table 5. Metal Experimental Sampling Time Intervals.

Minutes	Sampling Sites
0	All wells & Discharge
5	MNO & Discharge
15	All wells & Discharge
30	MNO & Discharge
50	All wells & Discharge
75	MNO & Discharge
100	All wells & Discharge
125	MNO & Discharge
150	MNO & Discharge
175	All wells & Discharge
200	MNO & Discharge
230	MNO & Discharge

Each sample was digested to eliminate the loss of metals due to humic precipitation. The digestion procedure is a modification of EPA standard method 3010A - Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy (July 1992, Appendix D). Modifications were the result of available equipment necessary to digest 200 samples per experiment on average and are listed in Appendix D following EPA method 3010.

The soil used in the test plot was found to contain significant concentration of easily extractable metals. Therefore, it was necessary to determine the leachable fraction as well. The leachable fraction is defined as the concentration of metals that would be removed with the normal flow of the water through the test plot. Using random samples taken from the final tracer experimentation, background leachable metal concentrations were determined for both well and surface flows. Leachable background concentrations determined are given in Table 6.

Table 6. Background concentration of leachable fraction of metals.

Metal	Well Background (ppb)	Surface Background (ppb)
Lead	83.8	60.0
Cadmium	16.0	16.6
Copper	140.0	74.0
Zinc	310.0	234.0

Variations Between Migration Experiments

While conducting the metal migration experiments, some alterations were made to the general procedures. Collection of the discharge samples also changed after the second migration experiment. The sample location of the two initial experiments was in the collection tank as a grab sample. For the remaining four experiments, discrete samples as shown in Table 5, were taken from a combined discharge location to better define the breakthrough characteristics of the test plot. In discussions concerning discharge samples, only the final four experiments were evaluated.

The greatest variation between experiments occurred during the fifth migration experiment. Two cracks were discovered in the test plot soil. The cracks were assumed to be a result of the moisture content becoming too low to maintain the integrity of the soil. The larger of the two cracks began 10.16 cm behind well C. It had a length 0.92 m which passed around the outside of well F and curved back into the test plot where it ended 12.7 cm in front of well I (see Figure 3). The crack was measured to 1.28 cm across at the widest point and approximately 2.56 cm deep. The second crack was located between well H and K. It was only 6.4 cm in length, but was 2.56 cm wide and 3.84 cm deep. A bromide tracer was applied to the test plot at the same slope as the migration experiments to determine the effect of the cracks in the test plot. The HRT after the crack was discovered was calculated to be 18.4 minutes, which was approximately 6 minutes less than the previously calculated HRT for the same slope and flow combination. The two replicated tracer experiments conducted under identical conditions had a variation of 13.4 minutes. Therefore, it was unclear how much the crack affected the final migration experiments based on HRT only. In the vertical migration study, as well as the monitoring of plant

concentrations, the presence of the crack may have affected the vertical location of the metals in the test plot.

Determination of Metal Sinks

Different literature sources have determined metals in roadsides have very shallow concentration gradients, generally within the top 10 to 15 cm (Lagerwerff and Specht, 1970 and Wang, 1980). Other researchers have examined the metal uptake capabilities of various plants (Fergusson, 1990 and Davis, 1992). These plants are possible sinks, as well as the soil itself. Both the vertical concentration gradient and the plant concentration were monitored to determine the location of the retained metals.

Plant Metal Uptake

The test plot vegetation consisted of the seed mix required by WSDOT for highways in western Washington (Appendix A). The mix consisted of red fescue, bent grass, rye and white Dutch clover. After tracer studies were completed, the white Dutch clover became the predominant species by choking the other grasses due to the constant lighting applied to the test plot. Background concentrations of metals in the plant material were taken both before and after the tracer study.

The test plot was divided into three sections to segregate the plant material. Each section was approximately 1 m with section 1 being located at the upper end of the test plot. The plant tissues were digested following the procedure determined by Havlin and Soltanpour, 1981 (see Appendix D). Samples consisted of leaf and stem material only. Four sample sets were taken during the course of the metal migration experiments. The final sample was taken after the final migration experiment and included a separate sampling of the root material to determine possible difference in absorbency.

Classification of the clover as an accumulator, indicator, or excludor was defined by use of a concentration factor (CF) determined by Chamberlain (1983). A CF of 1 is representative of an ideal indicator. A CF which is less than 1 indicates the plant exhibits an excluding tendency until a breakpoint concentration is reached. If the CF is greater than

1, the plant is assumed to be an accumulator with a larger CF representing a greater accumulation ability of the plant. To determine the classification of the clover, the soil concentration was acquired by the average of the 1 cm core samples taken in each grass sections of the test plot. The final clover analysis was utilized as the comparable plant concentration.

Vertical Migration

To determine the location of the metals retained in the test plot, depth samples were taken at 1, 5, 10, 15, and 20 cm. Samples were taken with a 2.56 cm diameter section of PVC piping cut to 1.28 cm thick. Twelve sites were sampled as illustrated in Figure 5. Appendix A lists the coordinates of each sample location. These sites were selected so that sampling did not occur directly over a well to insure representative samples of the entire test plot.

Each sample was weighed and dried. One gram of ground soil was digested in 100 ml of 1N HNO₃ and shaken for 24 hours. The digested samples were filtered, and digested according to EPA method 3010 described previously. All samples were analyzed using ICP Spectroscopy.

Soil cores were taken from the test plot on 5/4/95, approximately three weeks after the final migration study. During the coring, the test plot soil was discovered to be shallower than expected. The bentonite support layer had swollen forcing the actual depth of the test plot soil to average only 8 inches instead of the expected 10 inches. Therefore, any core with large amounts of bentonite was excluded due to the undetermined adsorption characteristics of the bentonite. At sites 3, 7, 9, 10, and 12, which were all located at the outer edges of the test plot (Figure 5), the 25 cm depth was also completely bentonite and was not sampled.

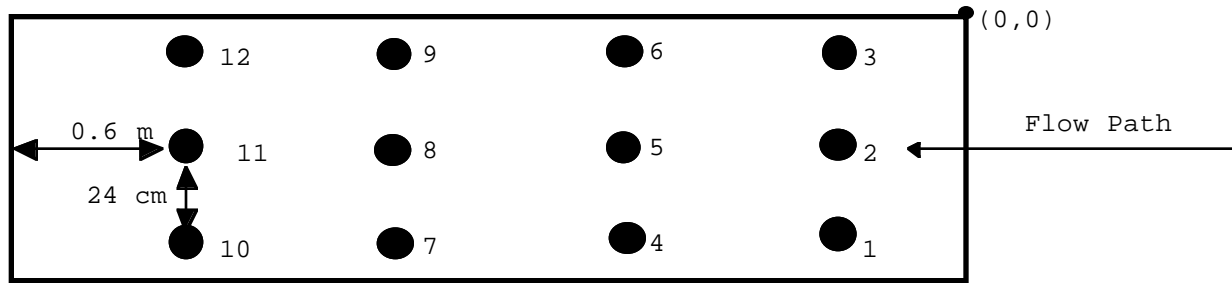


Figure 5. Soil Core Sampling Matrix

FINDINGS AND DISCUSSION

Hydraulic Characteristics of the Test Plot

The hydraulic characteristics of the test plot were defined to illustrate the effects of variations in both slope and flow. Hydraulic retention times were estimated utilizing a bromide tracer under six slope-flow combinations listed in Table 4. All bromide concentration data were tabulated according to their location in the test plot (see Appendix E). From each test, the overall breakthrough curve was developed for the final sampling well set (MNO). The breakthrough curve was used to determine the velocity, dispersion coefficient, and eventually the average hydraulic retention time.

During a simulated storm event, no shallow overland flow existed as sheet flow. Any observed surface flow existed as small channels that randomly appeared and disappeared. This observation, together with observations of a surface layer of soil that would best be described as “fluid” in appearance, indicated that a flow regime near the surface existed that is likely different than either classical surface flow or subsurface flow. This flow component is hereafter referred to as ‘seepage flow’ and has been described by Kadlec (1990).

From visual observations made during the tracer experiments, the main ‘seepage’ flow path traveled along the left side of the test plot for the initial 1.83 m, past wells F and I, and then returned to the center of the test plot within the remaining 1.22 m. A similar secondary flow path was also observed along the right edge of the test plot past wells D

and G. Well set DEF was low producing with an average sample volume of less than 10 ml per sample as compared to the other well sets at 30 to 50 ml per sample over the sample time interval. The total amount of tracer that passed through well set DEF never reached greater than 80% of the maximum feed concentration, C_o , of 50 mg/L. Well F was slightly more productive and maintained higher concentrations than either well D or E, illustrating the tendency for the flow to migrate to the left of the test plot. The increase in surface flow, decreased sample volume, and limited tracer concentrations were attributed to a more densely compacted soil at the 1.22 m location, resulting in a low conductivity zone. The general flow path was observed to migrate to either side of the test plot, moving around this low conductivity region.

Hydraulic Retention Times (HRT)

For ideal flow through systems, the average hydraulic retention time (HRT) is defined as the time required for half the total mass of a tracer ($C/C_o = 0.5$) to pass a specified point in a reactor. This specified point in the test plot was selected as well set MNO at 3 m from the inlet distribution plate.

The raw data from the tracer tests were fit with a predictive equation to assist in the estimation of HRT. A one-dimensional groundwater advection-dispersion equation (Equation 1.) was selected to describe the data (Bedient *et al.*, 1994).

$$D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}$$

C = concentration

D_x = dispersion coefficient along the x-axis

v_x = velocity

The analytical solution (Equation 2) derived by Ogata and Banks (1961) was used to allow direct application of the advection-dispersion equation. The basic assumptions of the Ogata-Banks solution are an infinite column with a zero background concentration, and the input tracer concentration at all locations are equal to the initial concentration, C_o (Bedient *et al.*, 1994).

$$\frac{C(t)}{C_o} = \frac{1}{2} \left[\operatorname{erf} \left(\frac{L - v_x t}{\sqrt{4D_x t}} \right) + \exp \left(\frac{v_x t}{L} \right) \operatorname{erf} \left(\frac{L + v_x t}{\sqrt{4D_x t}} \right) \right]$$

$C(t)$ = concentration of tracer at any time t .

C_o = initial concentration

L = linear distance where the concentration was measured

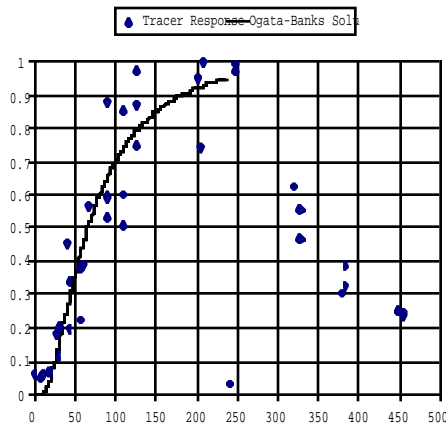
The velocity and dispersion coefficient were used as fitting parameter to minimize the residual sum of the squares between the raw data and the Ogata-Banks solution. The calculations were facilitated by Microsoft Excel solver to minimize the required fitting parameter. The initial concentration, C_o , was replaced by the maximum concentration observed at each well set, C^* . In most cases, C^* was greater than 85% of C_o and did not have any substantial effect on the values of velocity or the dispersion coefficient. For well sets D, E, and H, low concentrations and limited data due to low sample production made the estimation of the velocity and dispersion coefficients difficult. The use of C^* facilitated the determination of a velocity and a dispersion coefficient for these locations.

The Ogata-Banks solutions have been plotted with the raw data in Figure 6 (a-f) including the flow (F) and slope (S) for each particular tracer test. Figure 6 is a set of the breakthrough curves for the final well set (MNO) located at 3 m from the point of application. Figure 6a and 6e are replicate tracer tests at 0.38 L/min-m and 5% slope. Figure 6f is the required WSDOT slope and flow combination.

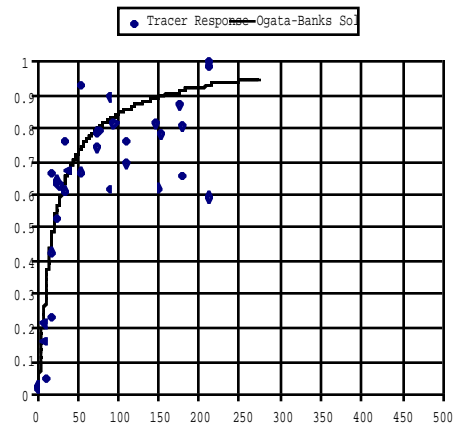
The variation in velocities was determined to be 0.03 cm/min. at the lowest slope and flow and 0.3/min. at the flow and slope of 3082 L/min-m and 17% respectively. Appendix E yields a complete list of the all velocities and dispersion coefficients calculated for each tracer test. The velocity increased with increasing distance (Figure 7) which indicated a non-linear increase in the head field of the test plot. The velocity also increased with an increase in either slope or flow as expected. The dispersion coefficient (D_x) was found to range between 2.6 cm²/sec. at the lowest slope - flow combination to 141.3 cm²/sec. at a slope - flow combination of 25% and 1.9 L/min-m. The dispersion

coefficients determine at the higher slope/flow combinations related to known field data.

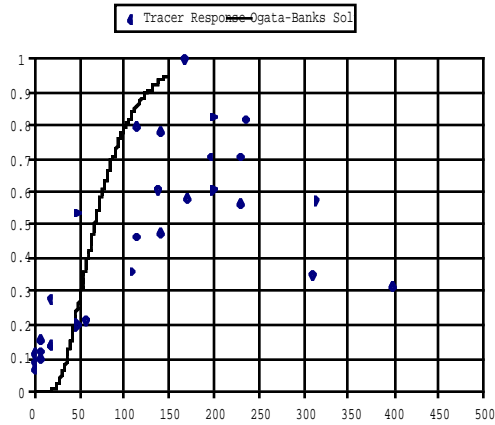
The dispersion coefficient was affected by the extensive variability of soil compaction,



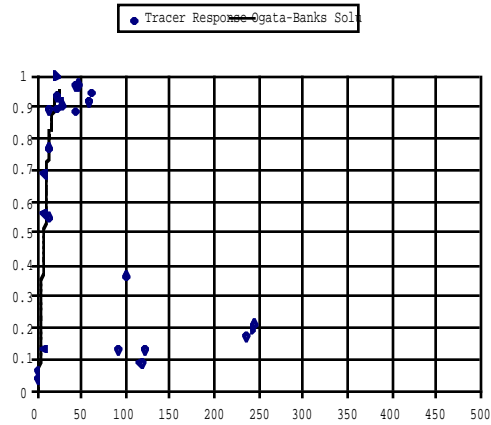
(a. F: 0.38 L/min-m; S:5%)



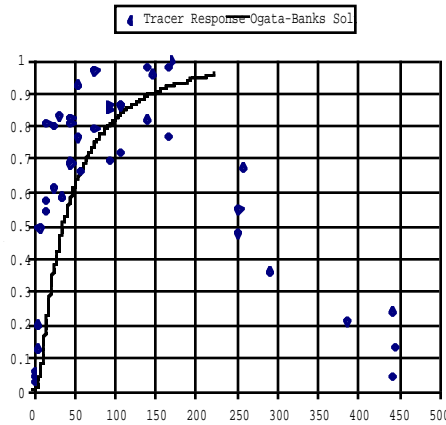
(b. F:1.9 L/min-m; S:5%)



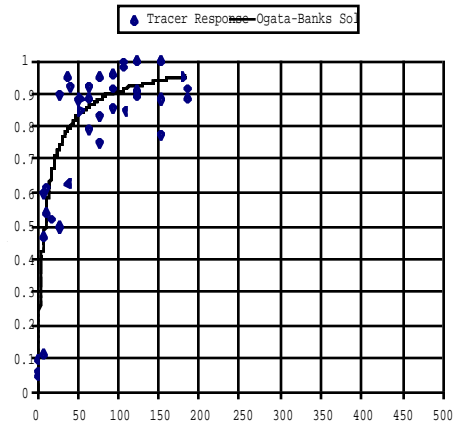
(c. F:0.38 L/min-m; S:25%)



(d. F: 1.9 L/min-m; S:25%)



(e. F: 0.38 L/min-m; S:5%)



(f. F:3.8 L/min-m; S:17%)

Figure 6. Overall breakthrough response of all tracer studies with the Ogata-Banks solution fit to the data. (a)run #4 (b)run #5 (c)run #6 (d)run #7 (e)run #8 (f)run #9

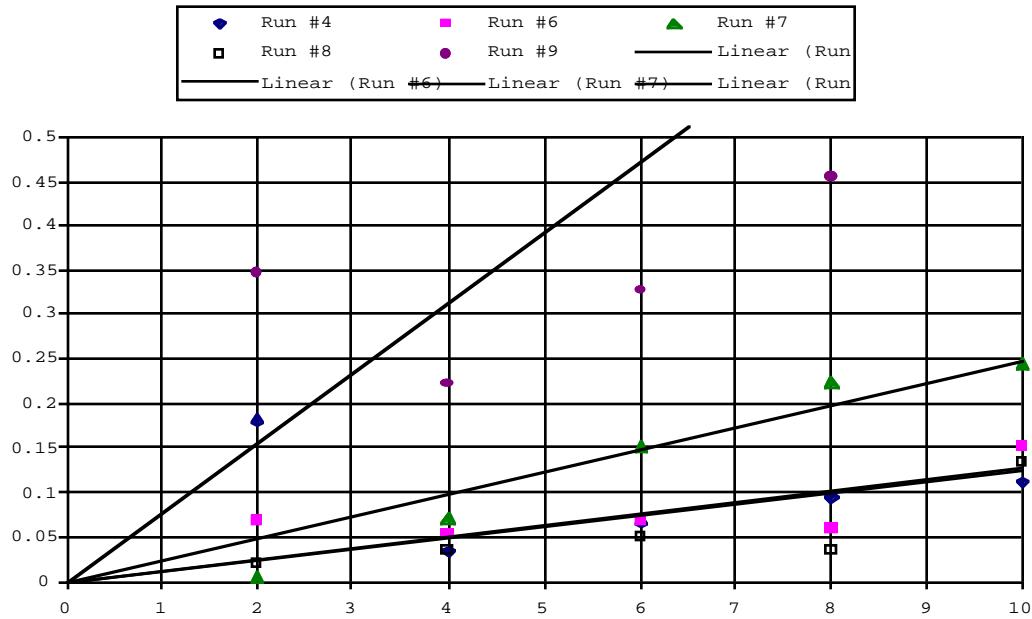


Figure 7. Estimated velocity versus linear distance of the test plot.

depth of the root zone, and general heterogeneity of the test plot which resulted in no discernible trend in the estimated values.

The average HRT for each slope and flow combination was determined by finding the inflection point of the Ogata-Banks solution. The inflection point was found by determining the time (t_{HRT}) in which the area from $t = 0$ to $t = t_{\text{HRT}}$ underneath the breakthrough curve is equal to the area from $t = t_{\text{HRT}}$ to $t = \infty$ above the curve. The trapezoid rule was used to numerically integrate both of these areas and to determine at what time they would be equal. The Ogata-Banks solution theoretically never reaches a value of unity; therefore, the integration was limited to $C(t)/C^* = 0.95$ as a maximum value.

The HRT was calculated for all six experimental combinations listed in Table 4. The overall HRT for each experimental combination of slope and flow was based on the 3 m well set (MNO). These values for HRT were also used to estimate the expected travel

times for the metals applied to the test plot. The determined values for the overall HRT as well as slope, flows, velocities, and dispersion coefficients used are listed in Table 7.

Table 7. HRT at well-set MNO for each experimental combination of slope and flow. Values of V_x and D_x are also included.

Run #	Slope (%)	Applied Flow (L/min-m)	V_x (cm/min.)	D_x (cm ² /sec.)	HRT (min.)
4	5	0.38	3.7	6.25	71.6
5	5	1.9	5.1	49.2	34.6
6	25	0.38	5.0	19.1	48.6
7	25	1.9	8.0	141	21.4
8	5	0.38	4.3	2.60	85.2
9	17	3.8	32.8	40.6	8.80

An increase in slope and/or flow was expected to decrease the overall average HRT for the test plot. The greatest percent change in average HRT of 88% was the result of a combined percent increase in slope and flow of 70% and 90%, respectively (run #4 versus run #9). With a similar increase in flow of 90% and a decrease in slope of 32% (run #6 versus run #9), only an 81% reduction occurred in the average HRT. No noticeable change due to decreasing the slope of the test plot. From these two comparisons, the flow is observed to have a greater affect on the average HRT of the test plot than changes in the slope. This assumption is also supported by the following. An 80% increase in slope at similar flows only induced a 32-38% decrease in the average HRT. Whereas, an identical percent increase of 80% in flow at similar slopes decreased the overall average HRT by 52-55%. Increases in both slope and flow were shown to decrease to overall HRT of the test plot, but flow was observed to have a more pronounced effect.

Two Dimensional Profiles of the Test Plot

The primary objective of utilizing the test plot was to determine the retention times from the roadside to the bottom of the grass strip. In the initial testing, the sample volume of each well was found to vary depending on the experimental conditions. Some wells would have large sample volume under one set of conditions and remain practically dry in

others. The same scenario was also true for the surface cups. As mentioned, at the 1.22 m well set location, the sample cups were always filled, indicating surface flow. The wells located at the 1.22 m set (DEF) would produce samples less frequently and at lower sample volumes than the other wells. It was expected that a low conductivity zone existed near the 1.22 m width.

Two dimensional plots (Figures 8 a-d) were developed to give a visual representation of the low conductivity zone was generated using data from tracer run #7 at a flow of 1.9 L/min-m and slope of 25%. This slope - flow combination was also used for the metal migration experiments. Figures 8a, 8b, 8c, and 8d are tracer concentration profiles at $t = 15, 50, 100,$ and 175 minutes, respectively. The color field indicates sub-surface tracer concentrations only. The limited number of data points of surface concentrations did not facilitate a complete two-dimensional analysis.

At the 15 minute time interval (8a), the tracer has entered the first well set located .61 m from the distribution plate. A large region of low concentration is seen at the location of the low conductivity zone. Another low concentration region is also seen to the left (facing “upstream”) of the test plot at 2.4 m from the flow distribution plate. Approximately 35 min. later (Figure 8b), the tracer concentration in wells M, N, and O at the 3 m location, is nearly equivalent to the feed concentration. However, both low concentration regions exhibited relatively low tracer levels. At the 100 min. time interval (Figure 8c), the second low concentration zone has finally been penetrated by the tracer, but has not quite reached the maximum concentration of 50 mg/L. Flow is still passing over the primary low conductivity zone though the majority of the test plot has reached 70 percent of the maximum concentration. Finally at 175 min. (Figure 8d), one side of the low conductivity region has been penetrated by the tracer but low concentrations remained in the center of the plot.

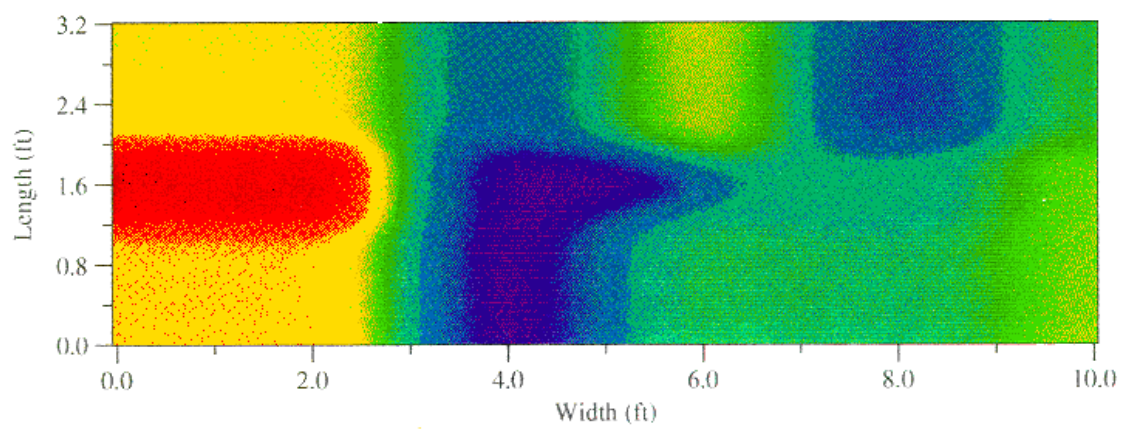
Metal Adsorption and Migration

Metal Adsorption

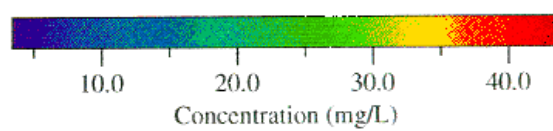
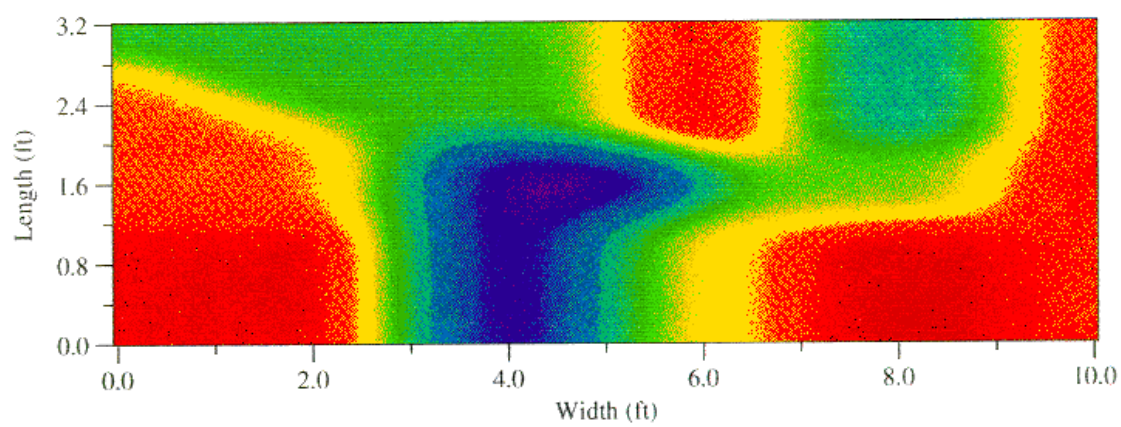
The data in Table 8 presents the equilibrium feed concentration determined in the competitive adsorption experiments. Total concentrations are calculated values based on the mass added (see Table 2.). Solid phase Zn was assumed to be near zero due to the inability to detect a significant difference between initial and final liquid phase concentration.

Table 8. Equilibrium feed concentrations for both solid and liquid phases.

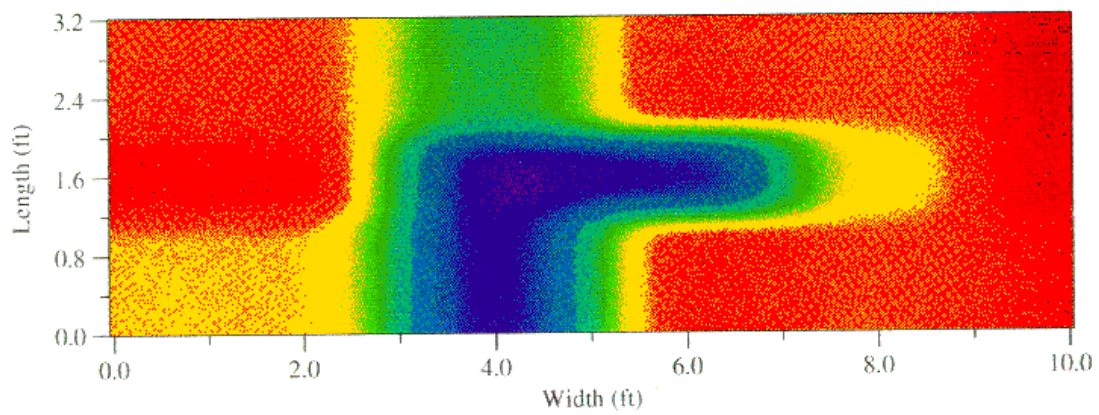
Component	Total Concentration (mg/L)	Liquid Phase (mg/L)	Solid Phase (mg/g)
Solids	250	N/A	N/A
Lead	2.099	0.33	9.94
Cadmium	0.08	0.05	0.06
Copper	0.22	0.03	8.88
Zinc	1.70	1.57	~ 0



(a)



(b)



(c) $t =$

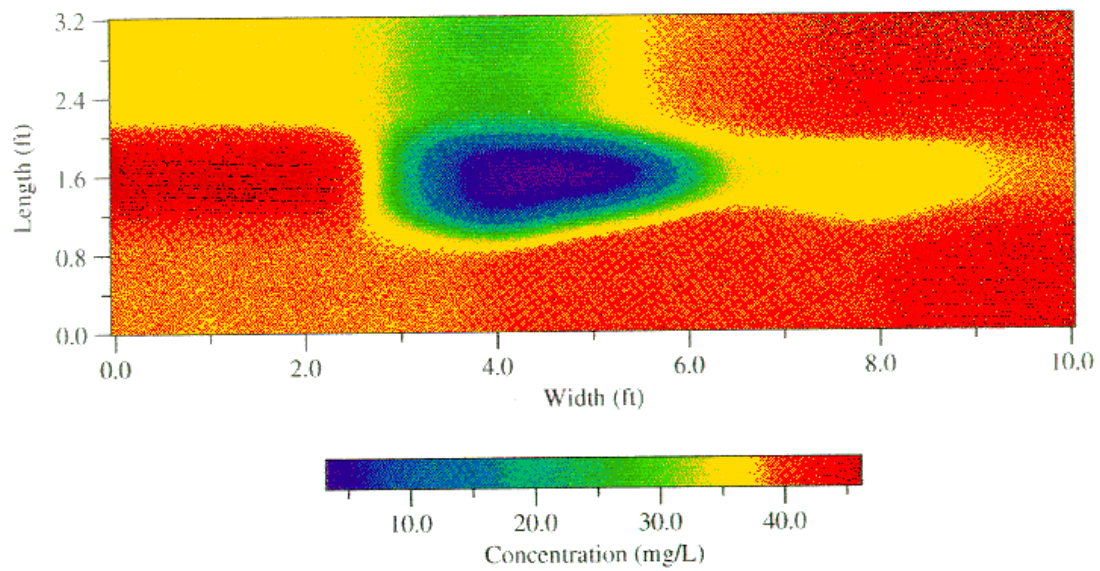


Figure 8. Two-dimensional tracer transport through the test plot (a) $t = 15$ minutes, (b) $t = 50$ minutes, (c) $t = 100$ minutes, (d) $t = 175$ minutes.

Wallowa Lake Sediment

Both the Wallowa Lake sediment and the test plot soil have a strong affinity to adsorb metals. Once applied to the test plot, the metals that remain partitioned to the Wallowa sediment are filtered out of the flow stream. Visual observation indicated that the Wallowa sediment was transported approximately 0.92 to 1.22 m down the length of the test plot. This observation was made based on minerals of distinctly different coloration in the Wallowa sediment that were not seen in the test plot soil.

The data in Figure 9a indicate that the Wallowa sediment had a higher solid phase capacity and K_d for lead than the test plot soil over the range of concentrations studied. Cadmium exhibited a higher K_d on the test plot soil than the sediment but the solid phase capacity was less for the test plot soil below an equilibrium liquid phase concentration of approximately 0.2 mg/L. Copper exhibited the same solid phase capacity and K_d for the test plot soil and sediment. Cadmium possessed the same K_d but a higher solid phase capacity on the sediment over all concentrations studied.

Test Plot Soil

The objective for the test plot soil adsorption isotherms was to estimate a soil distribution coefficient, K_d , used in calculating the linear equilibrium retardation factor, R , for each metal as listed in Table 9. The soil distribution coefficient is defined as the slope of a linear equilibrium isotherm. The bulk density of the soil and its effective porosity are required to determine the retardation coefficient as shown in Equation 3.

$$R = 1 + \left(\frac{\rho_b}{n} \right) K_d \quad 3$$

R = retardation coefficient

ρ_b = soil bulk density

n = porosity

K_d = soil distribution coefficient

For the soil in the test plot, the bulk density was estimated to be 108 lbm/ft³ and the porosity was assumed to be 0.3. The calculated retardation factors (Table 9) support the fact that the test plot has a high affinity for the metals to partition to its surface. The test plot is predicted to retain metals by a factor of at least 2000 times the calculated HRT, and up to 12,220 times for lead which has the highest adsorbing capacity (Table 9). The theoretical metal retention times (MRT) were calculated for each metal by applying the retardation coefficients to the Ogata-Banks solution (Equation 4). A metal concentration profile was then developed and the inflection point used to define MRT. Note that the retention times for the metals are given in days not minutes.

$$\frac{C(t)}{C_o} = \frac{1}{2} \left[\operatorname{erf} \left(\frac{RL - v_x t}{\sqrt{4RD_x t}} \right) + \exp \left(\frac{v_x t}{L} \right) \operatorname{erf} \left(\frac{RL + v_x t}{\sqrt{4RD_x t}} \right) \right] \quad 4$$

Table 9. Retardation factors and soil distribution coefficients for the test plot soil.

Metal	Soil Distribution coefficient, K_d (L/g)	Retardation Factor*	Estimated Retention Time* (days)
Lead	2.6192	12220	183
Cadmium	1.1133	5195	77
Copper	0.4319	2016	30
Zinc	0.5203	2428	36

* Calculated based on single-component conditions.

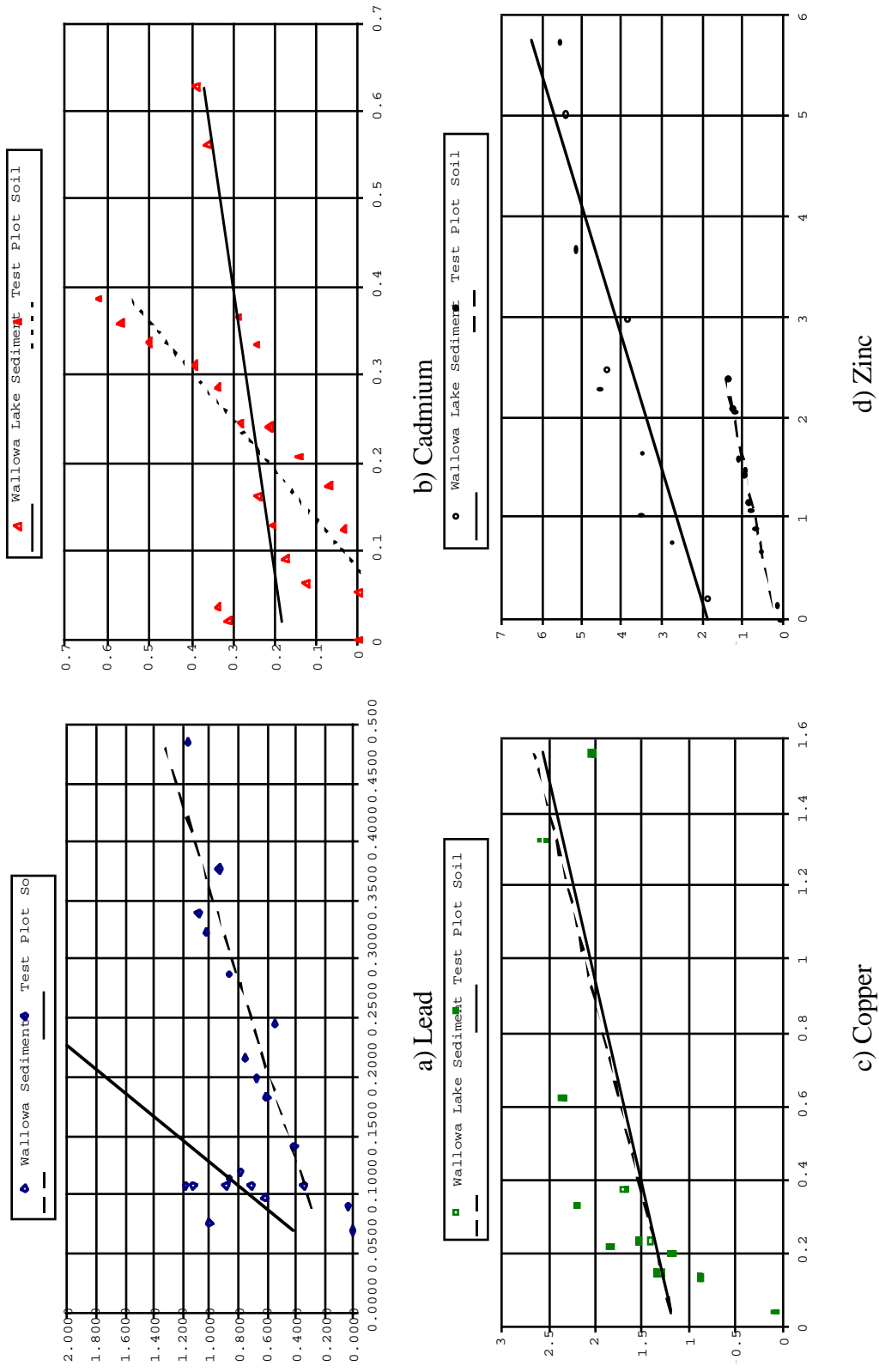


Figure 9. Single-solute adsorption isotherms developed for the Wallowa sediment and test plot soils.

The retardation factor order (lead>cadmium>zinc>copper) was somewhat unexpected with regard to copper relative to zinc and cadmium. Copper, like lead, has been shown in many studies to be strongly sorbed to soils while zinc is generally considered to have a relatively low adsorption affinity. The retardation factors indicate that both zinc and cadmium will be more retained than copper. Unfortunately, we could not confirm the predicted order of elution for copper due high background copper concentrations relative to the feed concentration. It should be understood, however, that the calculation of R and MRT are based on several simplifying assumptions that can lead to estimation errors.

Observed Inaccuracies in Prediction of MRT

The values of R and MRT are based on single solute adsorption isotherms and do not account for the potential impact of competitive adsorption on adsorption equilibria. In general, retardation estimates based on single solute equilibria data will be greater than those observed in a competitive adsorption environment. Under competitive conditions, one metal species will sorb more strongly to a site replacing more weakly sorbed metal species. The replaced metal would migrate down gradient at a greater rate resulting in an overall decreased retention time.

Other factors that are not accounted for in the application of equation 4 include;

- non-ideal flow,
- changes in flow characteristics as the site “ages”,
- vegetative uptake, and
- complex interactions between metal species and the soil in the grass strip and stormwater sediment.

Metal Migration Studies

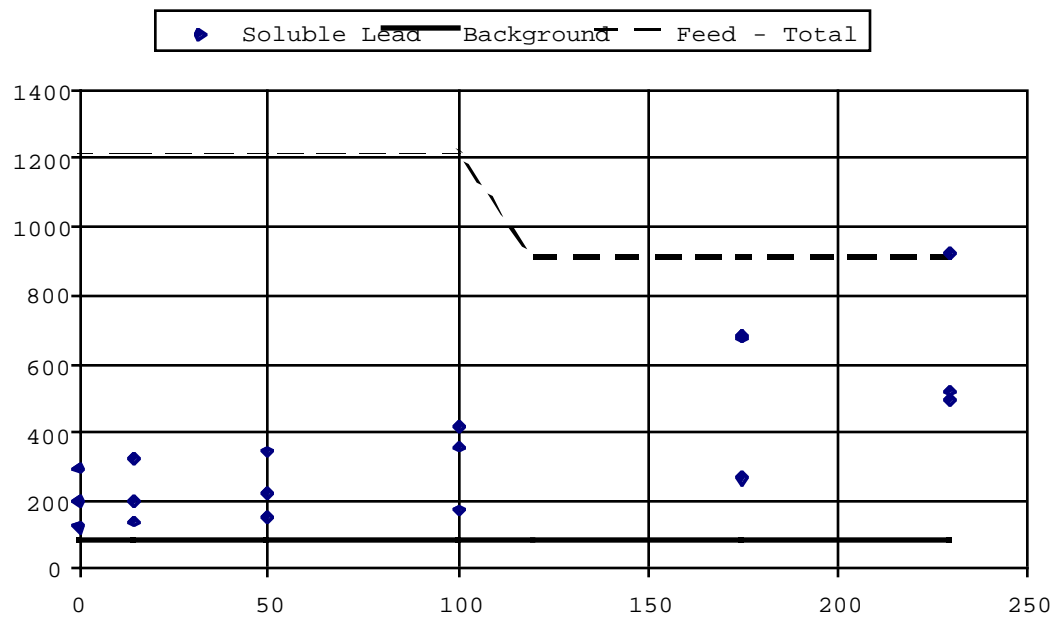
In the following discussion, the data generated during the first metal run (experiment #1) has not been included due to interference from humic acid precipitation.

This analytical problem was resolved following experiment #1 and all subsequent data is used, where appropriate, in the discussion.

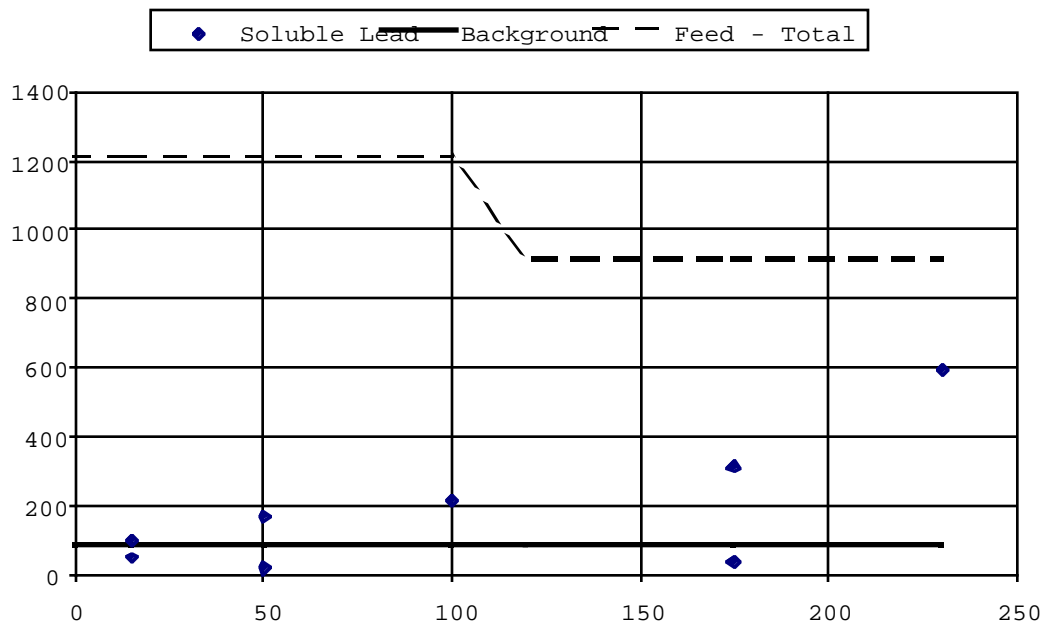
Intra Plot Observations

The two initial runs (experiments #1 and #2) were completed without detectable increases in the metal concentration. During experiment #3, an observable increase in lead concentration was observed at well set ABC (Figure 10.). Surface samples at DEF also exhibited an increase in lead concentration. Well set DEF remained below the background concentration for all metals. The average concentration for soluble lead, for example, was approximately 30 µg/L while the background soluble lead concentration over the entire grass strip was approximately 80 µg/L.

The remainder of the experiments (#4 - #6) yielded variable results as a function of the metal species, location within the grass strip, and cumulative run time. All metals remained below their respective feed concentrations at all well locations, including the most up-gradient well set (ABC. Evaluation of the copper data posed a unique challenge because the liquid phase background copper concentration (140 µg/L) was only 25 µg/L less than the average feed concentration of 165 µg/L. The data in Figure 11e does show that the average soluble copper concentration in well set ABC was less than the average feed concentration, however. All subsurface soluble metal concentrations remained below their respective feed concentrations throughout the study period. Lead was the only metal



a) Well Set ABC



b) Surface Cups DEF

Figure 10. Soluble lead versus time for the third migration experiment. flow = 1.9 L/min-m : Slope = 25%.

that exhibited a sustained increase in subsurface concentration. This increase occurred after a total elapsed run time of 1000 hours.

Grass Strip Discharge Observations

The data in Figure 11 indicates no discernible trend in the grass strip discharge concentrations for all metals over the entire study period. The concentration for each metal tended to vary about a sample mean and did not show any detectable increase, indicating that an obvious discharge “breakthrough” of metals did not occur. In addition, the average discharge concentrations over the entire study period remained below the feed concentrations. These observations indicate that, over the duration of the study period, the grass strip effectively detained the metals.

Comparisons between subsurface concentrations at well set ABC and the respective metal discharge concentrations indicate that the metals were migrating down gradient. This migration, however, was restricted to the upper section of the grass strip as well set ABC was the only set to exhibit sustained elevated metal concentrations compared to background values. A comparison of well set ABC and the grass strip discharge concentration is presented in Table 10. The sample means were evaluated using t-statistics and it was determined that the average discharge concentration of each metal was significantly less than the average subsurface (well set ABC) at the 95% confidence level.

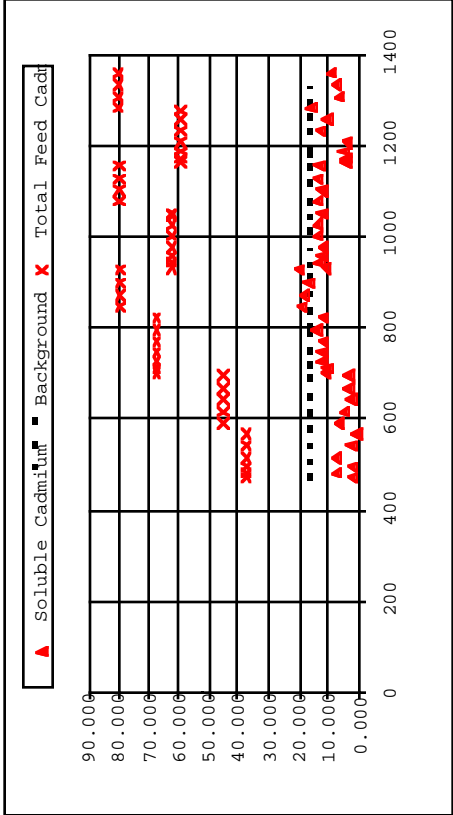
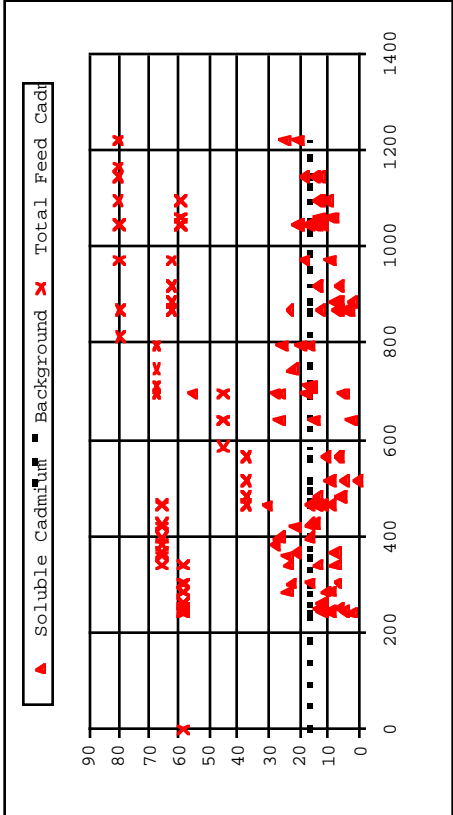
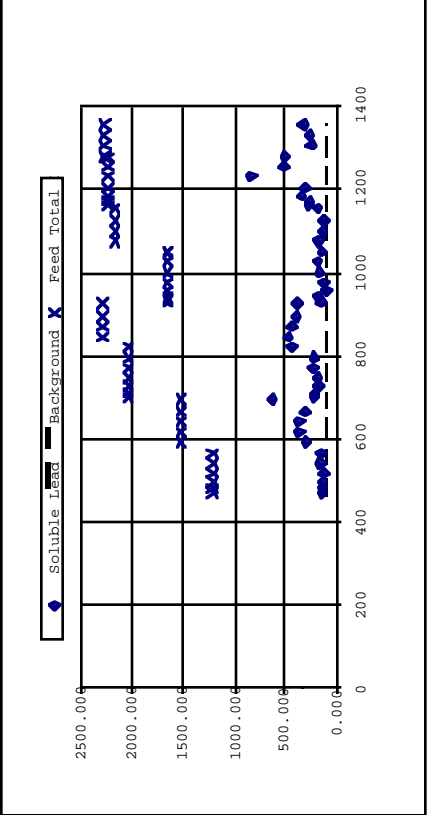
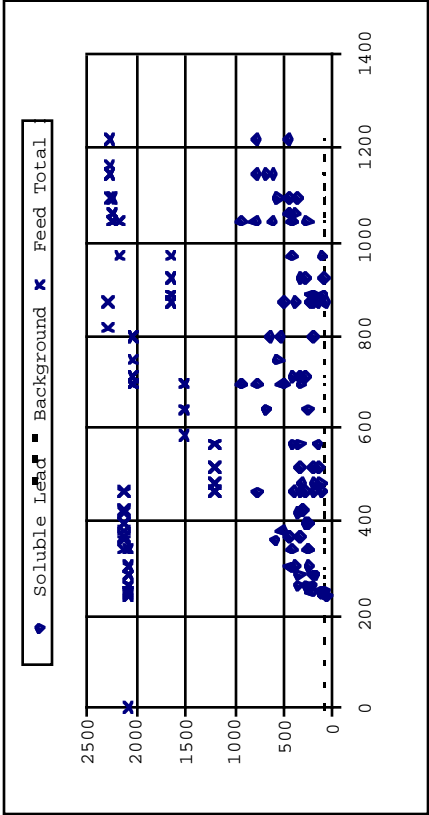
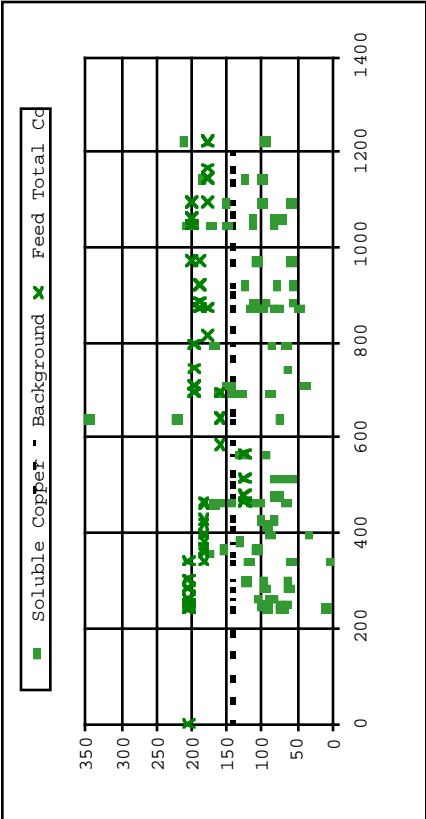
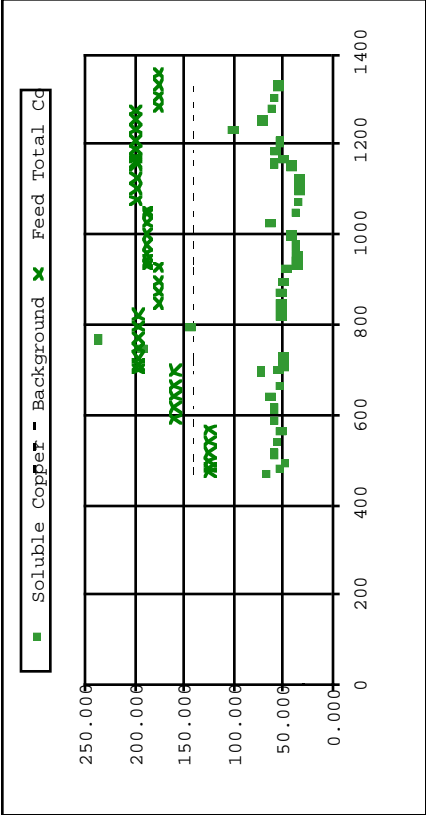


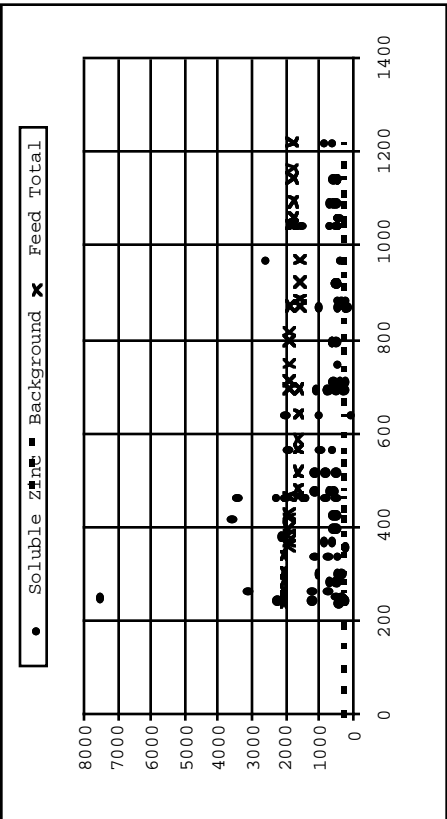
Figure 11. Metal concentration at the well set ABC and the test plot outfall.



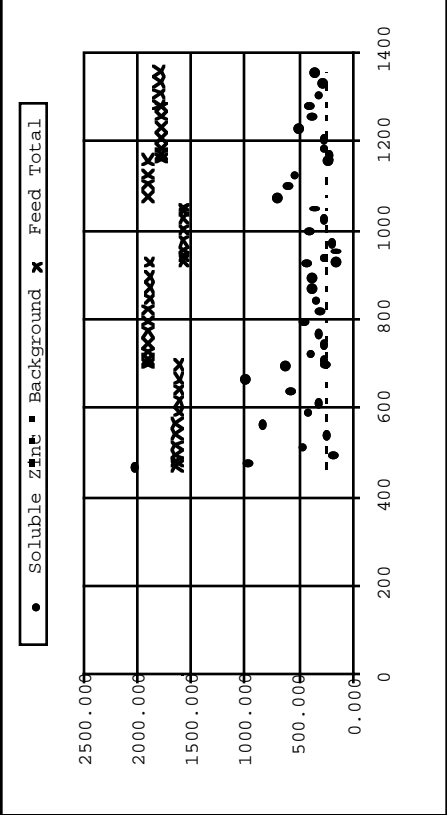
(a) copper - well set ABC



(b) copper - outfall



(a) zinc - well set ABC



(b) zinc - outfall

Figure 11 (cont.). Metal concentration at the well set ABC and the test plot outfall.

The observed differences between feed and discharge concentration was used to estimate the percent retained for each metal over the entire study period. The percent retained was calculated to be the difference between the applied mass and the discharged mass minus the background mass. The data in Table 10 indicate that the grass strip yielded excellent metal retention over the study period, ranging from a low of 84% for zinc and >99% for both cadmium and copper.

Table 10. Estimated metal retention times and percent retained for the test plot over the entire experimental period.

Metal	Well Set ABC Average ¹ (µg/L)	Discharge Average ² (µg/L)	Standard Deviation (ABC/Dis.)	Percent Retained (%)
Lead	379	270	211/149	93
Cadmium	14.3	9.2	8.06/5.14	>99
Copper	105	61.0	49.2/37.6	>99
Zinc	862	461	996/391	84

¹ Measured as soluble metals

² Measured as total Metals

Estimation and Description of Metal Sinks

Based on the evidence of significant metal retention an estimation of the fate of the metals was undertaken. This was accomplished by evaluating the metal concentration in the soil at various locations in the grass strip and the plant material. Recall that the fate of each metal is a function of complex interactions that include the relative adsorption affinities of the stormwater sediment and grass strip soil, competitive adsorption effects, and uptake into plant material. Indications of the significance of these interactions in defining the fate of each metal is presented in the following two subsections.

Soil Core Concentrations

Soil cores were collected at the end of the stormwater application experiments at 12 locations illustrated in Figure 5. These cores were then analyzed at depths of 1, 5, 10, and 20 cm. The results from the soil cores are illustrated in Figure 12. In general, for lead and zinc, the up-gradient sites (#1-#6) exhibited decreasing concentration with increasing depth. This general trend does not hold for sites #1 and #6, however, where zinc concentration increased with depth. This could be due to heterogeneous flow fields resulting from root zone affects, formation of macropores, or the heterogeneous nature of the soil. Visual observation of a crack in the soil at site #6 indicates that migration due to formation of macropores was likely.

The soil core concentration data was normalized by dividing the measured soil concentrations by the soil background concentration to enhance data evaluation. These data are presented in Figure 13. It can be seen that lead, cadmium, and zinc exhibited the highest soil concentrations in the first 1 cm depth and within the first 1 m of the influent stormwater flow path. These soil concentrations are corroborated by visual observations that indicated that the stormwater sediment was contained within the first 1 m of the test plot. This implies that the stormwater sediment likely contained a significant fraction of the metal contaminants and that retention of the sediment was an important mechanism for metal retention.

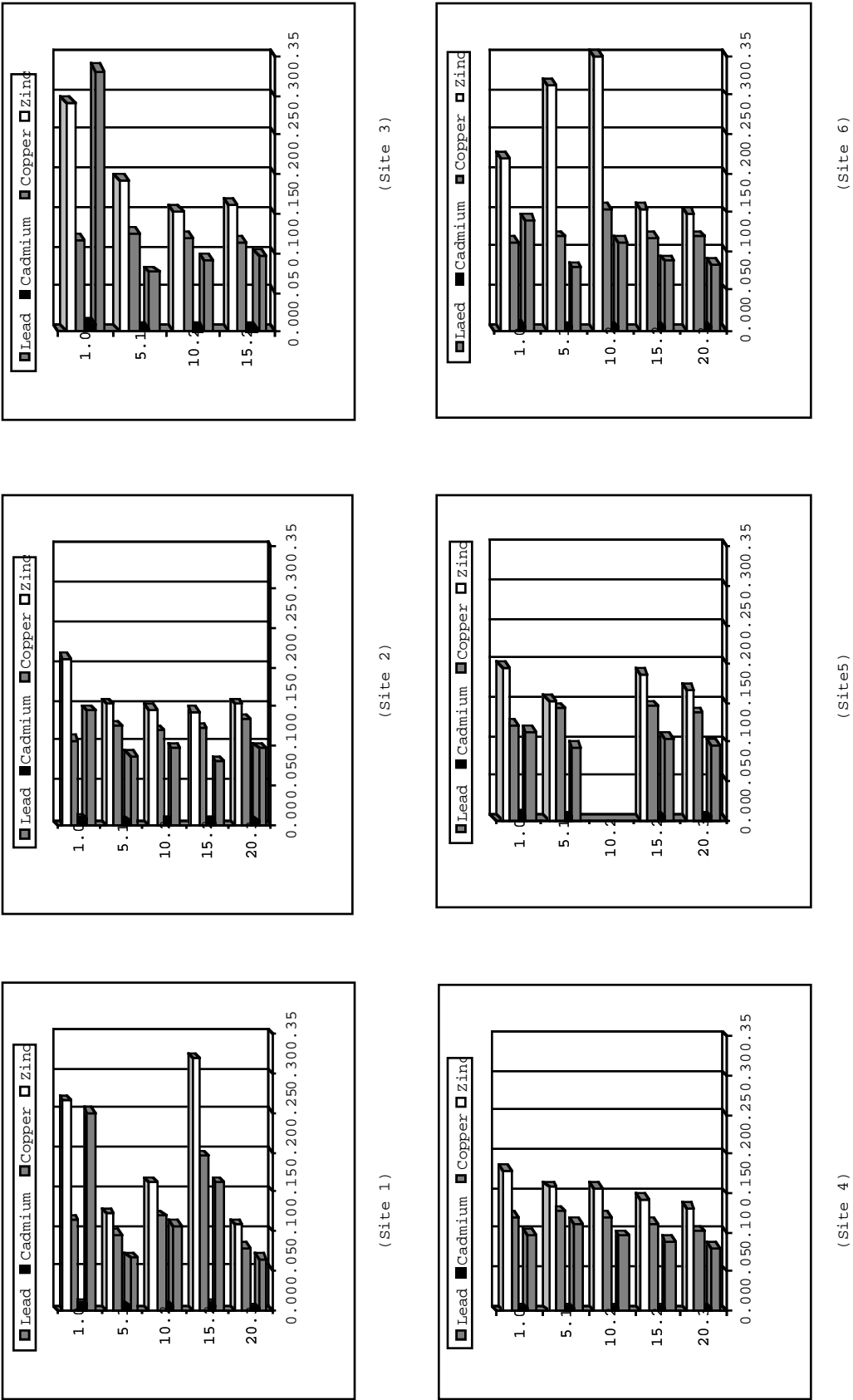
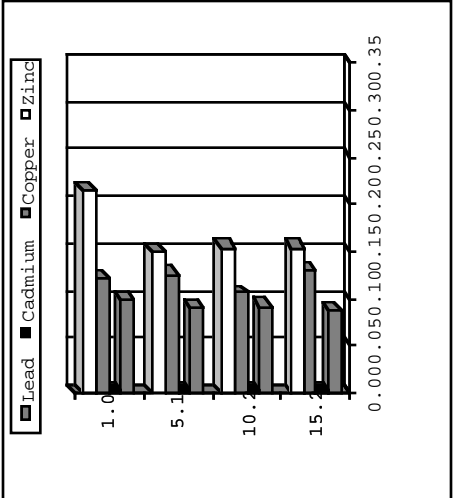
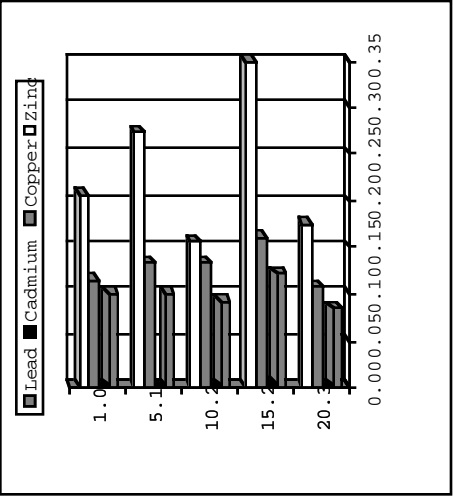


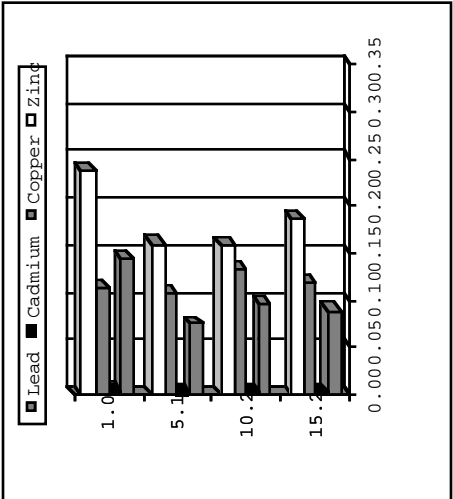
Figure12. Soil metal concentration as a function of depth for the test plot.



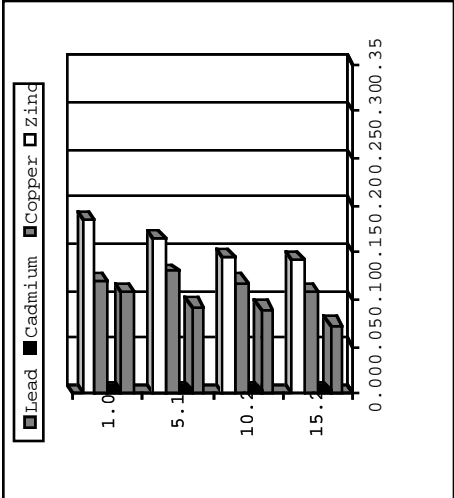
(Site 7)



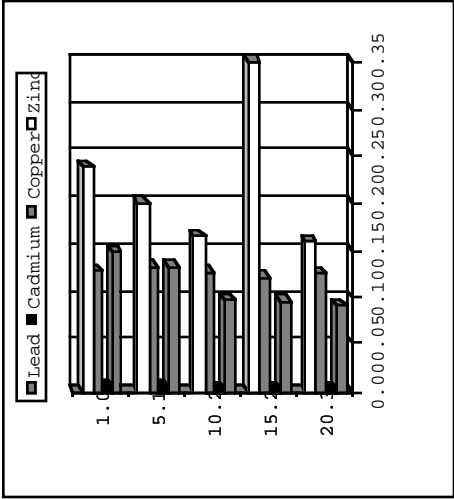
(Site 8)



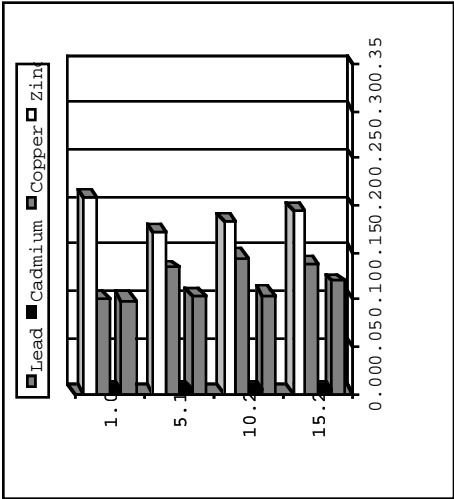
(Site 9)



(Site 10)

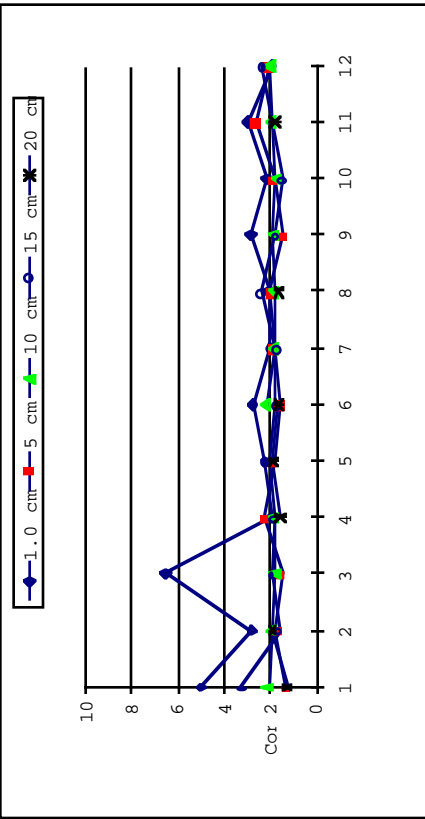


(Site 11)

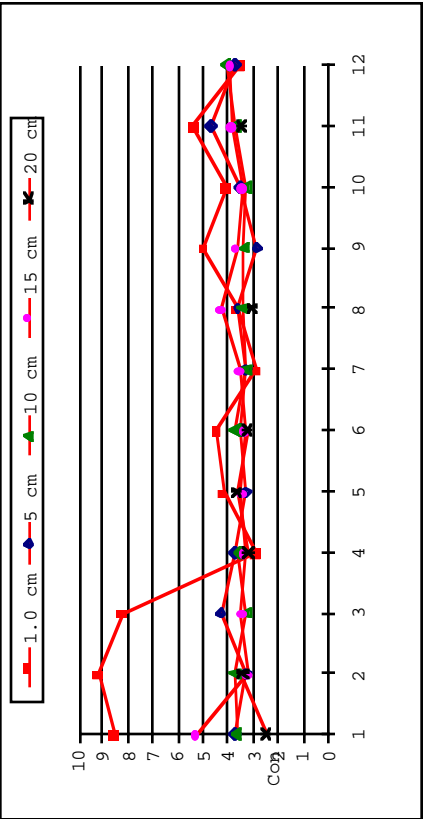


(Site 12)

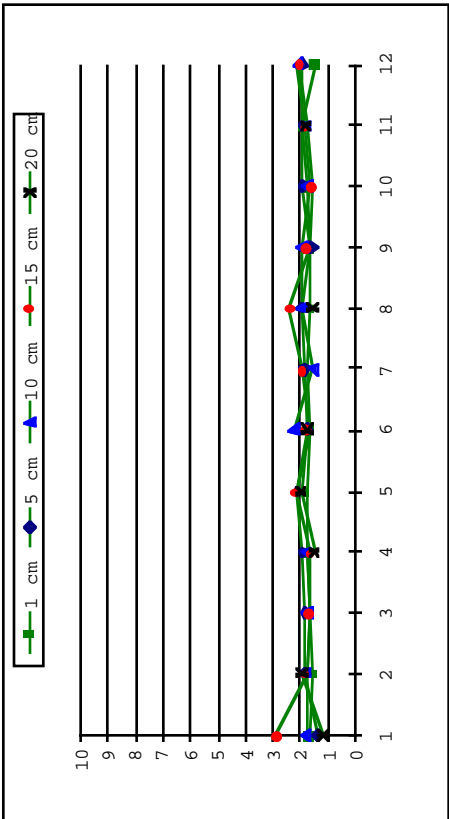
Figure 12 (cont.). Soil metal concentration as a function of depth for the test plot.



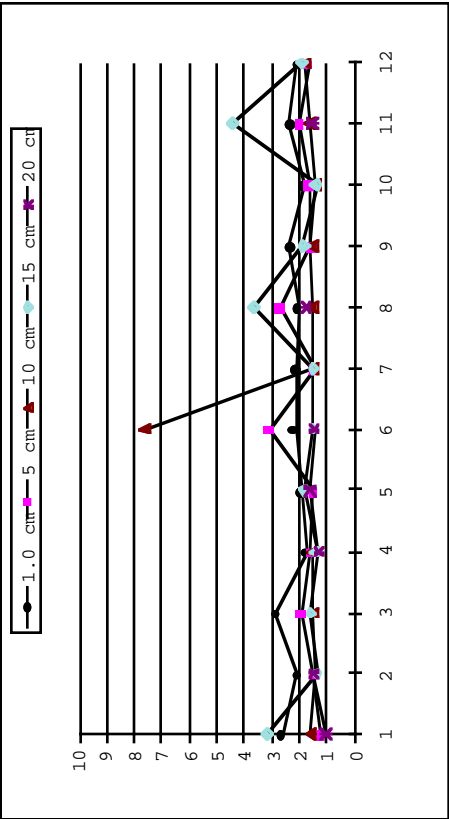
(a) lead



(b) cadmium



(c) copper



(d) zinc

Figure 13. Location of metal deposition in the test plot based on soil core data

Plant Uptake of Metals

During the hydraulic tracer study, the clover grew from an average height of 15.2 to 20.3 cm and maintained an average density of 1828 blades/ft². The overall health of the clover declined during the contaminant application period, however. The clover became thin, yellow in color, and did not grow to the original height realized during the tracer studies. The stunted growth initially occurred at the upper end of the test plot (section 1), and gradually migrated down-gradient during contaminant application testing. During root zone sampling it was discovered that the depth of the root zone was shallower in section 1 than in section 3. Following the final contaminant application, the grass density was estimated to be 1243 blades/ft². This gradual deterioration in vegetation health may have been a result of metal toxicity, this hypothesis was not confirmed, however.

The first two dates (8/15/94 and 2/6/95) presented in Figure 12 A-D, represent the period of time during which the vegetation species changed from predominantly grass to predominately clover. It is interesting to note that the cadmium concentration in the vegetation increased when clover began dominating. It is well known that cadmium is taken up by leafy species and this uptake is made evident in Figure 12D (Fergusson 1990). Zinc, copper, and lead exhibited the opposite trend, decreasing during clover dominance.

The roots were shown to contain more metal (dry weight basis) than the stems and leaf portion of the plants. Lead, which was previously shown to be contained in the first 1 m of the grass strip, shows the greatest plant concentration in the upper third of the test plot. Furthermore, the increase in lead vegetation concentration did not increase significantly until 4/21/95 and the highest concentrations were recorded in the roots. Many plants tend to exclude lead by enzymes found near their roots and this may explain the root accumulation of lead (Fergusson 1990). Conversely, zinc is shown to increase in concentration in plant material throughout the entire test period, a result of the higher degree of zinc mobility.

Based on the data presented in Table 11, it can be seen that vegetation planted in the test plot are “excludors” for the four metals tested. Excludor species will exhibit lower dry weigh plant concentrations than the surrounding soil, as was the case in this study. The “exclusion” of the metals from the plant material is made evident through the concentration factors (Table 11) calculated for three test strip sections by dividing the dry weight plant metal concentration by the dry weight soil metal concentration. Plant species that are defined as excludors will have CF values less than 1 while accumulator species would have CF values greater than one.

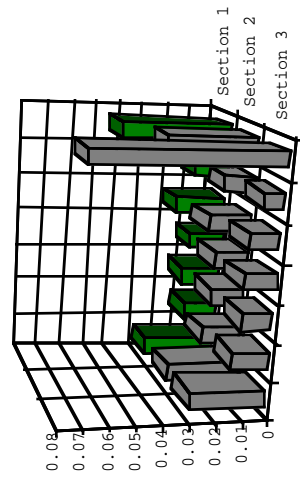
Table 11. Concentration Factors (CF) for the Vegetation Planted in the Test Plot.

	Lead			Cadmium		
	Plant (mg/g)	Soil (mg/g)	CF	Plant (mg/g)	Soil (mg/g)	CF
Section 1	0.0226	0.2417	0.0935	0.0010	0.0078	0.1282
Section 2	0.0118	0.1169	0.1009	0.0005	0.0032	0.1563
Section 3	0.0045	0.1185	0.0380	0.0000	0.0039	nd*
	Copper			Zinc		
	Plant (mg/g)	Soil (mg/g)	CF	Plant (mg/g)	Soil (mg/g)	CF
Section 1	0.0138	0.1118	0.1234	0.1223	0.2556	0.4785
Section 2	0.0116	0.1185	0.0979	0.1034	0.1974	0.5238
Section 3	0.0073	0.1158	0.0630	0.0695	0.2106	0.3300

* not defined

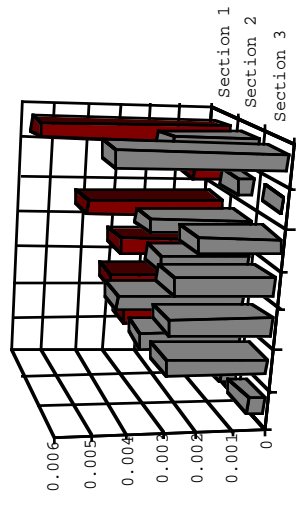


(A)

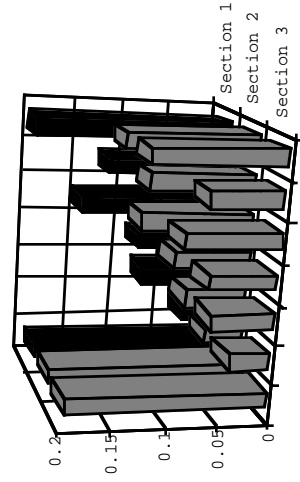


(B)

Figure 14. Monitoring Results for Plant Uptake of Metals. (A) Lead, (B) Cadmium, (C) Copper, and (D) Zinc.



(C)



(D)

CONCLUSIONS

Highway grass strips as a retention mechanism

Highway grass strips and shoulders can be effective metal retention mechanisms for the treatment of highway stormwater runoff. The full scale test plot migration experiments studied in this work indicated that greater than 84% of the zinc and 93 % of the lead applied was retained in the test plot. This metal retention was recorded over six simulated storm events with a cumulative stormwater application time of approximately 1350 minutes. Copper and cadmium exhibited >99% removal. No significant increase in concentration was observed at the test strip discharge for any of the metals and, with the exception of copper, all metal concentrations remained well below their respective feed concentration. Since no obvious metal breakthrough occurred at the test plot discharge or in upgradient wells, it was not possible to accurately estimate metal retention time.

The primary metal retention mechanism appeared to be entrapment of the stormwater sediment which had a high adsorption affinity for the metals studied. Additional retention through adsorption on the test strip soil also occurred, but was difficult to quantify due to background concentrations that were high relative to the mass of metal applied during the testing period.

Plant Classification

The WSDOT seed mix exhibited excludor characteristics for the metal contaminants studied. The clover began dominating during the inert tracer experiments and its' general health deteriorated with respect to distance and time in conjunction with each successive metal migration experiment.

Test Plot Hydraulic Detention Times

The test plot hydraulic detention times, calculated at different slope/flow combinations, ranged from 8.8 minutes for a slope of 17% and flow of 3.8 L/min • m to and average of 78.4 minutes at a slope/flow combination of 5% and 0.38 L/min • m. Relative to percent

changes in slope and flow, a change in flow has a greater effect on hydraulic detention time than an equivalent percent change in slope. Dispersion coefficients, calculated using the Ogata-Banks solution of the one-dimensional groundwater advection-dispersion equation, were similar to published field data.

RECOMMENDATIONS

Based on the results presented, highway grass strips can act as an effective retention mechanism for heavy metals and sediment. It should be noted that the duration of experimentation was short relative to the runoff time frame of a field site. However, significant metal breakthrough was not observed at the most up-gradient monitoring point located 0.6m from the stormwater application point. Based on this result it can be hypothesized that significant metal retention would be anticipated for times significantly greater than the experimental period. The current design limits for highway safety shoulders appear to be satisfactory for metal retention. However, to enhance the retention potential of grass strips, the degree of slope must be selected with respect to estimations of the highest flows that may occur. If possible, higher flows should be related to the shallowest slope possible to allow for the longest hydraulic retention times and, subsequently, the retention time for the metals. Regions which experience lower flows can be allowed a wider variations in their slopes, though lower slopes would still enhance the retention potential.

In the construction of grass strips, a high degree of compaction increases the amount of surface flow that occurs in a grass strip. The greater the amount of surface flow results in a shorter average HRT for the slope. In areas which high intensity storms are commonplace, lower degrees of compaction would allow for more subsurface flows and longer average HRTs. In the tracer study, a low conductivity zone was discovered in the test plot which was observed to force flow around and above it.

The roadways can also be designed to enhance the retention potential of the grass strips. Limiting the amount of channeling of the stormwater before it is diverted to the roadside and grass strips decreases flow rates which increase retention times. Planting of thick vegetation and use of permeable soils are expected to increase the retention potential by allowing greater filtration and increasing the preference of the metal to sorb to the soils and biota of the grass strip.

Further study into the effects of organic matter, plant speciation, ground cover, and moisture conditions on metal retention would greatly enhance the understanding of metal migration and ultimately refine the design of grass strips to their highest retention potential. It is recommended, based on the positive results obtained herein, that a long-term field study be initiated to extend the data base to other soil types and a longer flow history. This would afford a means of evaluating variability that can only be experienced in the field and result in a confirmation of the laboratory studies, lending support to design criteria.

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APPENDICES

APPENDIX A - TABLES

Table 1.A. Constituents of Highway Runoff - Ranges of Average Values Reported in
the Literature (Barrett et al. 1992)

Constituent	Concentration (mg/L unless noted)	Load (kg/ha/year)	Load (kg/ha/event)
SOLIDS			
Total	437 - 1147		58.2
Dissolved	356	148	
Suspended	45 - 798	314 - 11,862	84 - 107.6
Volatile, dissolved	131		
Volatile, suspended	4.3 - 79	45 - 961	0.89 - 28.4
Volatile, total	57 - 242	179 - 2518	10.5
METALS (totals)			
Zn	0.056 - 0.929	0.22 - 10.40	0.004 - 0.025
Cd	ND - 0.04	0.0072 - 0.037	0.002
As	0.058		
Ni	0.053	0.07	
Cu	0.022 - 7.033	0.030 - 4.67	0.0063
Fe	2.429 - 10.3	4.37 - 28.81	0.56
Pb	0.073 - 1.78	0.08 - 21.2	0.008 - 0.22
Cr	ND - 0.04	0.012 - 0.010	0.0031
Mg	1.062		
Hg (x 10 ⁻³)	3.22	0.007	0.0007
NUTRIENTS			
Ammonia, as N	0.07 - 0.22	1.03 - 4.60	
Nitrite, as N	0.013 - 0.25		
Nitrate, as N	0.306 - 1.4		
Nitrite + Nitrate	0.15 - 1.636	0.8 - 8.00	0.078
Organic, as N	0.965 - 2.3		
TKN	0.335 - 55.0	1.66 - 31.95	0.17
Nitrogen, asN	4.1	9.80	0.02 - 0.32
Phosphorous, as P	0.113 - 0.998	0.6 - 8.23	
MISCELLANEOUS			
Total coliforms number/100 mL	570 - 6200		

Fecal coliforms number/100 mL	50 - 590		
Sodium		1.95	
Chloride		4.63 - 1344	
pH	7.1 - 7.2		
Total Organic Carbon	24 - 77	31.3 - 342.1	0.88 - 2.35
COD	14.7 - 272	128 - 3868	2.90 - 66.9
BOD 5	12.7 - 37	30.60 - 164	0.98
Polyaromatic Hydrocarbons (PAH)		0.005 - 0.018	
Oil and Grease	2.7 - 27	4.85 - 767	0.09 - 0.16
Specific Conductance (µmohs/cm @ 25° C)	337 - 500		
Turbidity (JTU)	84 - 127		
Turbidity (NTU)	19		

Table 2.A. Highway Contaminant Concentrations Determined by Driscoll 1990.
(Site Median Concentrations in mg/L for Monitored Storm Events)

State Code	Location Description	SS	VSS	TOC	COD	TKN	PO ₄ - P	Cu	Pb	Zn
WA-5	Montsano SR-12	126	21	3	46	0.64	0.168	0.036	0.175	0.100
WA-6	Pasco SR-12	101	25	10	114	3.32	0.476	0.025	0.101	0.325
WA-9	Pullman SR-270E	104	21	17	60	0.75	0.428	0.026	0.130	0.099
WA-1	Seattle I-5	93	26	13	106	0.9	0.217	0.037	0.451	0.382
WA-2	Seattle SR-520	244	59	33	145	1.09	0.415	0.072	1.065	0.280
WA-4	Snoqualmie Pass I-90	43	9	2	41	0.38	0.123	0.025	0.065	0.071
WA-7	Spokane I-90	119	29	10	156	1.69	0.865	0.041	0.173	2.892
WA-3	Vancouver I-205	34	9	7	32	0.60	0.098	0.017	0.046	0.040

Table 3.A. WSDOT seed mix for western Washington

Type of Seed	% by weight	Min % Pure Seed	Min % Germination
Red Fescue	40	39.2	90
Colonial Bentgrass	10	9.8	85
Perennial Rye	40	39.2	90

White Dutch Clover	10	9.8	90
Weed Seed	-----	0.50 max.	-----
Inert Material	-----	1.50 max.	-----

Supplied by Davenport Seed Co., Davenport, Washington - Ms. Karen Rinabout

Table 4A Location of Soil Cores Taken from the Test Plot.

Location #	X-Coordinate	Y-Coordinate
1	29.25	2
2	19.5	2
3	9.75	2
4	29.25	4
5	19.5	4
6	9.75	4
7	29.25	6
8	19.5	6
9	9.75	6
10	29.25	8
11	19.5	8
12	9.75	8

The origin is taken to be the left point of application of the flow stream.

Table 5.A. Estimated Seepage Velocities and Dispersion Coefficients for Tracer Study.

	Set ABC		Set DEF		Set GHI		Set JKL		Set MNO	
	Dx		Vx		Dx		Vx		Dx	
	cm ² /min	cm/min	cm ² /min	cm/min	cm ² /min	cm/min	cm ² /min	cm/min	cm ² /min	cm/min
Run #4	5.51	140.66	1.08	38.37	2.06	198.07	29.17	232.72	3.40	375.1
Run #5	0.80	156.17	3.01	1413.98	4.80	1353.60	6.10	601.55	4.74	3448.8
Run #6	2.02	365.76	1.66	316.71	2.03	559.09	1.83	581.94	4.62	1148.2
Run #7	0.21	922.25	2.19	739.88	4.63	1740.63	6.83	2486.73	7.43	8477.4
Run #8	0.65	221.76	1.08	125.79	1.55	13.01	1.08	1324.89	4.03	156.1
Run #9	10.54	303.61	6.72	58.62	9.99	501.30	13.80	980.22	30.47	2445.3

APPENDIX B. - FIGURES

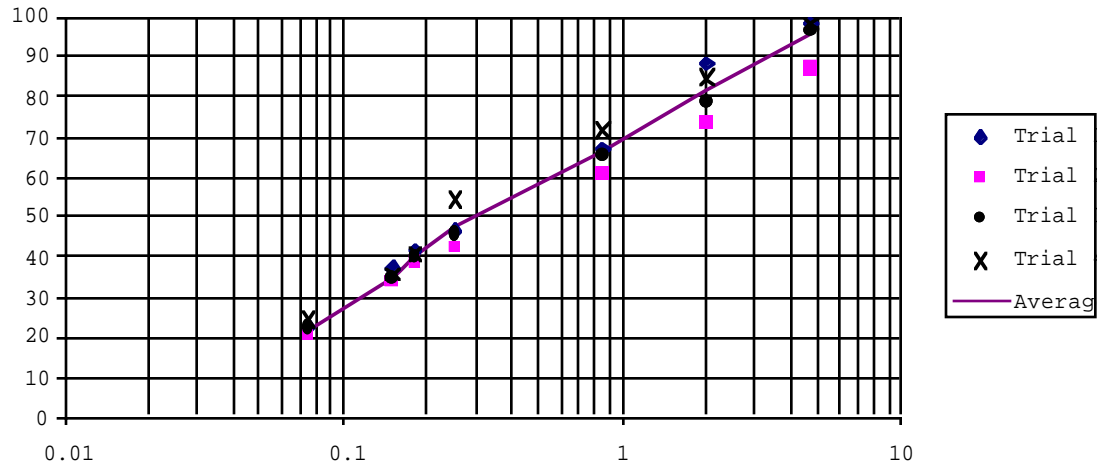


Figure B.1 Particle Size Distribution for Test Plot Soil - Sieve Analysis

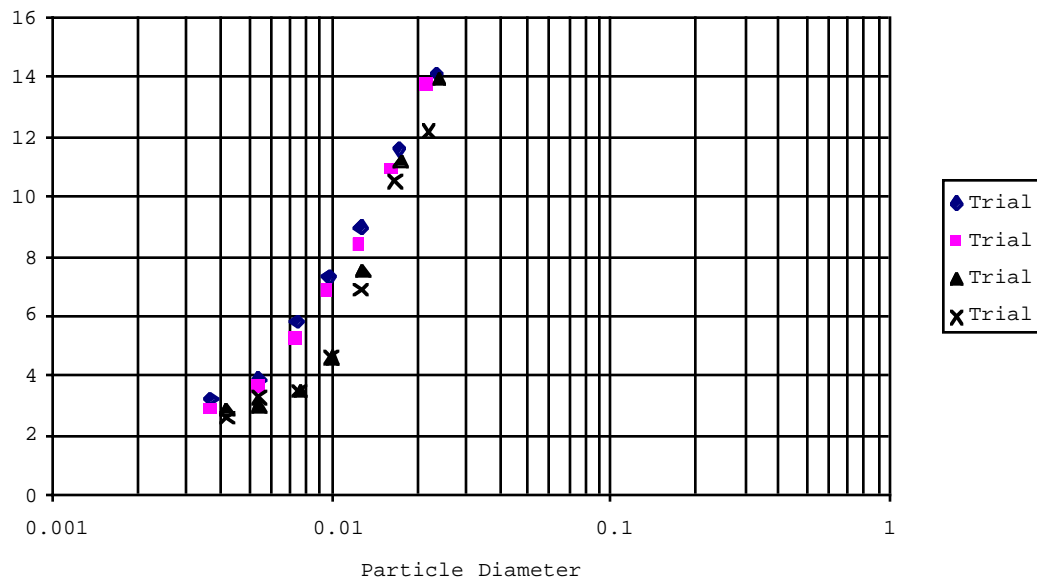


Figure B.2 Particle Size Distribution for Test Plot Soil - Hydrometer Analysis

APPENDIX C - DESIGN STORM HYDROGRAPHS

Table C.1 General Hydrograph Data for all Design Storms

Rainfall Type:	IA					
Time of Concentration	5 minutes					
Area	40.5 m2					
	Olympia 4-lane	Olympia 2-lane	Olympia 1-lane	Seattle 4-lane	Seattle 2-lane	Seattle 1-lane
Precipitation (cm)	4.55	4.55	4.55	3.25	3.25	3.25
Total Volume (L)	2067	1170	568	1397	783	352
Max. Flow (L/min)	7.82	4.42	2.21	5.44	3.06	1.53
Min. Flow (L/min)	0.17	0.00	0.00	0.17	0.00	0.00
Intensity (cm/hr)	2.05	0.21	0.21	0.15	0.15	1.81
First Flush Volume (L)	413	235	114	280	155	72
Wash-out Volume (L)	829	469	227	560	314	140
Trail-off Volume (L)	829	469	227	560	314	140

Table C.2 Hydrograph for Olympia 4-lane Design Storm

time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)
10	0.00	430	3.06	850	1.19	1270	1.02	1690	0
20	0.00	440	4.25	860	1.36	1280	1.02	1700	0
30	0.00	450	4.42	870	1.36	1290	1.02	1710	0
40	0.00	460	6.12	880	1.36	1300	1.02	1720	0
50	0.00	470	7.82	890	1.36	1310	1.02	1730	0
60	0.00	480	7.82	900	1.36	1320	1.02	1740	0
70	0.00	490	5.61	910	1.36	1330	0.85	1750	0
80	0.00	500	3.40	920	1.36	1340	0.85	1760	0
90	0.00	510	3.40	930	1.36	1350	0.85	1770	0
100	0.00	520	3.23	940	1.36	1360	0.85	1780	0
110	0.17	530	3.06	950	1.36	1370	0.85	1790	0
120	0.34	540	3.06	960	1.36	1380	0.85	1800	0
130	0.34	550	2.55	970	1.02	1390	0.85	1810	0
140	0.51	560	2.04	980	0.85	1400	0.85	1820	0
150	0.51	570	2.04	990	0.85	1410	0.85	1830	0
160	0.68	580	2.04	1000	0.85	1420	0.85	1840	0
170	0.68	590	2.04	1010	0.85	1430	0.85	1850	0
180	0.68	600	2.04	1020	0.85	1440	0.34	1860	0
190	0.85	610	2.04	1030	1.02	1450	0	1870	0
200	0.85	620	1.87	1040	1.19	1460	0	1880	0
210	0.85	630	1.87	1050	1.19	1470	0	1890	0
220	0.85	640	1.87	1060	1.19	1480	0	1900	0
230	1.02	650	1.87	1070	1.19	1490	0	1910	0
240	1.02	660	1.87	1080	1.19	1500	0	1920	0
250	1.02	670	1.70	1090	1.02	1510	0	1930	0
260	1.19	680	1.53	1100	1.02	1520	0	1940	0
270	1.19	690	1.53	1110	1.02	1530	0	1950	0
280	1.19	700	1.53	1120	1.36	1540	0	1960	0
290	1.19	710	1.53	1130	1.02	1550	0	1970	0
300	1.19	720	1.53	1140	0.68	1560	0	1980	0
310	1.53	730	1.53	1150	1.02	1570	0	1990	0
320	1.87	740	1.53	1160	1.02	1580	0	2000	0
330	1.87	750	1.53	1170	1.02	1590	0	2010	0
340	2.04	760	1.53	1180	1.02	1600	0	2020	0
350	2.04	770	1.53	1190	1.02	1610	0	2030	0
360	2.04	780	1.53	1200	1.02	1620	0	2040	0
370	2.04	790	1.36	1210	1.02	1630	0		
380	1.87	800	1.19	1220	1.02	1640	0		
390	1.87	810	1.19	1230	1.02	1650	0		
400	1.87	820	1.19	1240	1.02	1660	0		
410	1.87	830	1.19	1250	1.02	1670	0		

Table C.3. Hydrograph for Olympia 2-lane Design Storm

time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)
10	0.00	420	1.02	830	0.68	1240	0.51	1650	0.00
20	0.00	430	1.70	840	0.68	1250	0.51	1660	0.00
30	0.00	440	2.38	850	0.68	1260	0.51	1670	0.00
40	0.00	450	2.55	860	0.85	1270	0.51	1680	0.00
50	0.00	460	3.40	870	0.85	1280	0.51	1690	0.00
60	0.00	470	4.42	880	0.85	1290	0.51	1700	0.00
70	0.00	480	4.42	890	0.85	1300	0.51	1710	0.00
80	0.00	490	3.23	900	0.85	1310	0.51	1720	0.00
90	0.00	500	1.87	910	0.85	1320	0.51	1730	0.00
100	0.00	510	1.87	920	0.85	1330	0.51	1740	0.00
110	0.00	520	1.87	930	0.85	1340	0.51	1750	0.00
120	0.17	530	1.70	940	0.85	1350	0.51	1760	0.00
130	0.17	540	1.70	950	0.85	1360	0.51	1770	0.00
140	0.34	550	1.53	960	0.85	1370	0.51	1780	0.00
150	0.34	560	1.19	970	0.68	1380	0.51	1790	0.00
160	0.34	570	1.19	980	0.51	1390	0.51	1800	0.00
170	0.34	580	1.19	990	0.51	1400	0.51	1810	0.00
180	0.51	590	1.19	1000	0.51	1410	0.51	1820	0.00
190	0.51	600	1.19	1010	0.51	1420	0.51	1830	0.00
200	0.51	610	1.19	1020	0.51	1430	0.51	1840	0.00
210	0.51	620	1.02	1030	0.51	1440	0.17	1850	0.00
220	0.51	630	1.02	1040	0.68	1450	0.00	1860	0.00
230	0.51	640	1.02	1050	0.68	1460	0.00	1870	0.00
240	0.51	650	1.02	1060	0.68	1470	0.00	1880	0.00
250	0.68	660	1.02	1070	0.68	1480	0.00	1890	0.00
260	0.68	670	1.02	1080	0.68	1490	0.00	1900	0.00
270	0.68	680	0.85	1090	0.68	1500	0.00	1910	0.00
280	0.68	690	0.85	1100	0.51	1510	0.00	1920	0.00
290	0.68	700	0.85	1110	0.51	1520	0.00	1930	0.00
300	0.68	710	0.85	1120	0.68	1530	0.00	1940	0.00
310	0.85	720	0.85	1130	0.51	1540	0.00	1950	0.00
320	1.02	730	0.85	1140	0.34	1550	0.00	1960	0.00
330	1.19	740	0.85	1150	0.51	1560	0.00	1970	0.00
340	1.19	750	0.85	1160	0.51	1570	0.00	1980	0.00
350	1.19	760	0.85	1170	0.51	1580	0.00	1990	0.00
360	1.19	770	0.85	1180	0.51	1590	0.00	2000	0.00
370	1.19	780	0.85	1190	0.51	1600	0.00	2010	0.00
380	1.02	790	0.85	1200	0.51	1610	0.00	2020	0.00
390	1.02	800	0.68	1210	0.51	1620	0.00	2030	0.00
400	1.02	810	0.68	1220	0.51	1630	0.00	2040	0.00
410	1.02	820	0.68	1230	0.51	1640	0.00		

Table C.4. Hydrograph for Olympia 1-lane Design Storm

time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)
10	0.00	420	0.51	830	0.34	1240	0.34	1650	0.00
20	0.00	430	0.85	840	0.34	1250	0.34	1660	0.00
30	0.00	440	1.19	850	0.34	1260	0.34	1670	0.00
40	0.00	450	1.19	860	0.34	1270	0.34	1680	0.00
50	0.00	460	1.70	870	0.34	1280	0.34	1690	0.00
60	0.00	470	2.21	880	0.34	1290	0.34	1700	0.00
70	0.00	480	2.21	890	0.34	1300	0.34	1710	0.00
80	0.00	490	1.70	900	0.34	1310	0.34	1720	0.00
90	0.00	500	1.02	910	0.34	1320	0.34	1730	0.00
100	0.00	510	1.02	920	0.34	1330	0.17	1740	0.00
110	0.00	520	0.85	930	0.34	1340	0.17	1750	0.00
120	0.00	530	0.85	940	0.34	1350	0.17	1760	0.00
130	0.00	540	0.85	950	0.34	1360	0.17	1770	0.00
140	0.00	550	0.68	960	0.34	1370	0.17	1780	0.00
150	0.17	560	0.68	970	0.34	1380	0.17	1790	0.00
160	0.17	570	0.68	980	0.17	1390	0.17	1800	0.00
170	0.17	580	0.68	990	0.17	1400	0.17	1810	0.00
180	0.17	590	0.68	1000	0.17	1410	0.17	1820	0.00
190	0.17	600	0.68	1010	0.17	1420	0.17	1830	0.00
200	0.17	610	0.51	1020	0.17	1430	0.17	1840	0.00
210	0.17	620	0.51	1030	0.34	1440	0.00	1850	0.00
220	0.34	630	0.51	1040	0.34	1450	0.00	1860	0.00
230	0.34	640	0.51	1050	0.34	1460	0.00	1870	0.00
240	0.34	650	0.51	1060	0.34	1470	0.00	1880	0.00
250	0.34	660	0.51	1070	0.34	1480	0.00	1890	0.00
260	0.34	670	0.51	1080	0.34	1490	0.00	1900	0.00
270	0.34	680	0.51	1090	0.34	1500	0.00	1910	0.00
280	0.34	690	0.51	1100	0.34	1510	0.00	1920	0.00
290	0.34	700	0.51	1110	0.34	1520	0.00	1930	0.00
300	0.34	710	0.51	1120	0.34	1530	0.00	1940	0.00
310	0.51	720	0.51	1130	0.34	1540	0.00	1950	0.00
320	0.51	730	0.51	1140	0.34	1550	0.00	1960	0.00
330	0.51	740	0.51	1150	0.17	1560	0.00	1970	0.00
340	0.51	750	0.51	1160	0.34	1570	0.00	1980	0.00
350	0.51	760	0.51	1170	0.34	1580	0.00	1990	0.00
360	0.51	770	0.51	1180	0.34	1590	0.00	2000	0.00
370	0.51	780	0.51	1190	0.34	1600	0.00		
380	0.51	790	0.34	1200	0.34	1610	0.00		
390	0.51	800	0.34	1210	0.34	1620	0.00		
400	0.51	810	0.34	1220	0.34	1630	0.00		
410	0.51	820	0.34	1230	0.34	1640	0.00		

Table C.5. Hydrograph for Seattle 4-lane Design Storm

time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)
10	0.00	420	1.36	830	0.85	1240	0.68	1650	0.00
20	0.00	430	2.04	840	0.85	1250	0.68	1660	0.00
30	0.00	440	2.89	850	0.85	1260	0.68	1670	0.00
40	0.00	450	2.89	860	1.02	1270	0.68	1680	0.00
50	0.00	460	4.08	870	1.02	1280	0.68	1690	0.00
60	0.00	470	5.27	880	1.02	1290	0.68	1700	0.00
70	0.00	480	5.44	890	1.02	1300	0.68	1710	0.00
80	0.00	490	3.91	900	1.02	1310	0.68	1720	0.00
90	0.00	500	2.38	910	1.02	1320	0.68	1730	0.00
100	0.00	510	2.38	920	1.02	1330	0.68	1740	0.00
110	0.00	520	2.21	930	1.02	1340	0.51	1750	0.00
120	0.00	530	2.04	940	1.02	1350	0.51	1760	0.00
130	0.17	540	2.21	950	1.02	1360	0.51	1770	0.00
140	0.17	550	1.87	960	1.02	1370	0.51	1780	0.00
150	0.34	560	1.53	970	0.68	1380	0.51	1790	0.00
160	0.34	570	1.53	980	0.51	1390	0.51	1800	0.00
170	0.34	580	1.53	990	0.51	1400	0.51	1810	0.00
180	0.34	590	1.53	1000	0.51	1410	0.51	1820	0.00
190	0.51	600	1.53	1010	0.51	1420	0.51	1830	0.00
200	0.51	610	1.36	1020	0.51	1430	0.51	1840	0.00
210	0.51	620	1.36	1030	0.68	1440	0.34	1850	0.00
220	0.51	630	1.36	1040	0.85	1450	0.00	1860	0.00
230	0.51	640	1.36	1050	0.85	1460	0.00	1870	0.00
240	0.51	650	1.36	1060	0.85	1470	0.00	1880	0.00
250	0.68	660	1.36	1070	0.85	1480	0.00	1890	0.00
260	0.68	670	1.19	1080	0.85	1490	0.00	1900	0.00
270	0.68	680	1.02	1090	0.68	1500	0.00	1910	0.00
280	0.68	690	1.02	1100	0.68	1510	0.00	1920	0.00
290	0.68	700	1.02	1110	0.68	1520	0.00	1930	0.00
300	0.85	710	1.02	1120	1.02	1530	0.00	1940	0.00
310	1.02	720	1.02	1130	0.68	1540	0.00	1950	0.00
320	1.19	730	1.02	1140	0.51	1550	0.00	1960	0.00
330	1.19	740	1.02	1150	0.68	1560	0.00	1970	0.00
340	1.19	750	1.02	1160	0.68	1570	0.00	1980	0.00
350	1.36	760	1.02	1170	0.68	1580	0.00	1990	0.00
360	1.36	770	1.02	1180	0.68	1590	0.00	2000	0.00
370	1.36	780	1.02	1190	0.68	1600	0.00	2010	0.00
380	1.19	790	1.02	1200	0.68	1610	0.00	2020	0.00
390	1.19	800	0.85	1210	0.68	1620	0.00	2030	0.00
400	1.19	810	0.85	1220	0.68	1630	0.00	2040	0.00
410	1.36	820	0.85	1230	0.68	1640	0.00		0.00

Table C.6. Hydrograph for Seattle 2-lane Design Storm

time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)
10	0.00	420	0.68	830	0.51	1240	0.34	1650	0.00
20	0.00	430	1.19	840	0.51	1250	0.34	1660	0.00
30	0.00	440	1.70	850	0.51	1260	0.34	1670	0.00
40	0.00	450	1.70	860	0.51	1270	0.34	1680	0.00
50	0.00	460	2.38	870	0.51	1280	0.34	1690	0.00
60	0.00	470	3.06	880	0.51	1290	0.34	1700	0.00
70	0.00	480	3.06	890	0.51	1300	0.34	1710	0.00
80	0.00	490	2.21	900	0.51	1310	0.34	1720	0.00
90	0.00	500	1.36	910	0.51	1320	0.34	1730	0.00
100	0.00	510	1.36	920	0.51	1330	0.34	1740	0.00
110	0.00	520	1.19	930	0.51	1340	0.34	1750	0.00
120	0.00	530	1.19	940	0.51	1350	0.34	1760	0.00
130	0.00	540	1.19	950	0.51	1360	0.34	1770	0.00
140	0.00	550	1.02	960	0.51	1370	0.34	1780	0.00
150	0.00	560	0.85	970	0.34	1380	0.34	1790	0.00
160	0.17	570	0.85	980	0.34	1390	0.34	1800	0.00
170	0.17	580	0.85	990	0.34	1400	0.34	1810	0.00
180	0.17	590	0.85	1000	0.34	1410	0.34	1820	0.00
190	0.17	600	0.85	1010	0.34	1420	0.34	1830	0.00
200	0.34	610	0.85	1020	0.34	1430	0.34	1840	0.00
210	0.34	620	0.68	1030	0.34	1440	0.00	1850	0.00
220	0.34	630	0.68	1040	0.51	1450	0.00	1860	0.00
230	0.34	640	0.68	1050	0.51	1460	0.00	1870	0.00
240	0.34	650	0.85	1060	0.51	1470	0.00	1880	0.00
250	0.34	660	0.85	1070	0.51	1480	0.00	1890	0.00
260	0.34	670	0.68	1080	0.51	1490	0.00	1900	0.00
270	0.34	680	0.68	1090	0.51	1500	0.00	1910	0.00
280	0.34	690	0.68	1100	0.34	1510	0.00	1920	0.00
290	0.34	700	0.68	1110	0.34	1520	0.00	1930	0.00
300	0.51	710	0.68	1120	0.51	1530	0.00	1940	0.00
310	0.51	720	0.68	1130	0.34	1540	0.00	1950	0.00
320	0.68	730	0.68	1140	0.34	1550	0.00	1960	0.00
330	0.68	740	0.68	1150	0.34	1560	0.00	1970	0.00
340	0.68	750	0.68	1160	0.34	1570	0.00	1980	0.00
350	0.68	760	0.68	1170	0.34	1580	0.00	1990	0.00
360	0.68	770	0.68	1180	0.34	1590	0.00	2000	0.00
370	0.68	780	0.68	1190	0.34	1600	0.00	2010	0.00
380	0.68	790	0.51	1200	0.34	1610	0.00	2020	0.00
390	0.68	800	0.51	1210	0.34	1620	0.00	2030	0.00
400	0.68	810	0.51	1220	0.34	1630	0.00	2040	0.00
410	0.68	820	0.51	1230	0.34	1640	0.00		0.00

Table C.7. Hydrograph for Seattle 1-lane Design Storm

time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)	time (min)	Design Runoff (Lpm)
10	0.00	420	0.34	830	0.17	1240	0.17	1650	0.00
20	0.00	430	0.68	840	0.17	1250	0.17	1660	0.00
30	0.00	440	0.85	850	0.17	1260	0.17	1670	0.00
40	0.00	450	0.85	860	0.34	1270	0.17	1680	0.00
50	0.00	460	1.19	870	0.34	1280	0.17	1690	0.00
60	0.00	470	1.53	880	0.34	1290	0.17	1700	0.00
70	0.00	480	1.53	890	0.34	1300	0.17	1710	0.00
80	0.00	490	1.19	900	0.34	1310	0.17	1720	0.00
90	0.00	500	0.68	910	0.34	1320	0.17	1730	0.00
100	0.00	510	0.68	920	0.34	1330	0.17	1740	0.00
110	0.00	520	0.68	930	0.34	1340	0.00	1750	0.00
120	0.00	530	0.68	940	0.34	1350	0.00	1760	0.00
130	0.00	540	0.68	950	0.34	1360	0.00	1770	0.00
140	0.00	550	0.51	960	0.34	1370	0.00	1780	0.00
150	0.00	560	0.34	970	0.17	1380	0.00	1790	0.00
160	0.00	570	0.34	980	0.00	1390	0.00	1800	0.00
170	0.00	580	0.34	990	0.00	1400	0.00	1810	0.00
180	0.00	590	0.34	1000	0.00	1410	0.00	1820	0.00
190	0.00	600	0.34	1010	0.00	1420	0.00	1830	0.00
200	0.00	610	0.34	1020	0.00	1430	0.00	1840	0.00
210	0.00	620	0.34	1030	0.17	1440	0.00	1850	0.00
220	0.00	630	0.34	1040	0.17	1450	0.00	1860	0.00
230	0.00	640	0.34	1050	0.17	1460	0.00	1870	0.00
240	0.00	650	0.34	1060	0.17	1470	0.00	1880	0.00
250	0.17	660	0.34	1070	0.17	1480	0.00	1890	0.00
260	0.17	670	0.34	1080	0.17	1490	0.00	1900	0.00
270	0.17	680	0.34	1090	0.17	1500	0.00	1910	0.00
280	0.17	690	0.34	1100	0.17	1510	0.00	1920	0.00
290	0.17	700	0.34	1110	0.17	1520	0.00	1930	0.00
300	0.17	710	0.34	1120	0.34	1530	0.00	1940	0.00
310	0.34	720	0.34	1130	0.17	1540	0.00	1950	0.00
320	0.34	730	0.34	1140	0.00	1550	0.00	1960	0.00
330	0.34	740	0.34	1150	0.17	1560	0.00	1970	0.00
340	0.34	750	0.34	1160	0.17	1570	0.00	1980	0.00
350	0.34	760	0.34	1170	0.17	1580	0.00	1990	0.00
360	0.34	770	0.34	1180	0.17	1590	0.00	2000	0.00
370	0.34	780	0.34	1190	0.17	1600	0.00	2010	0.00
380	0.34	790	0.34	1200	0.17	1610	0.00	2020	0.00
390	0.34	800	0.17	1210	0.17	1620	0.00	2030	0.00
400	0.34	810	0.17	1220	0.17	1630	0.00	2040	0.00
410	0.34	820	0.17	1230	0.17	1640	0.00		0.00

APPENDIX D. - ANALYTICAL PROCEDURES

Procedure 1.D - Isotherm Analysis

1. Add soil mass (m_s) of approximately 5 grams to 19 125 ml Nalgene bottles
2. Add DI water to the isotherm reactor bottles according to the following table and shake for 24 hours to allow the dried soil to become completely wetted.

Reactor Bottle ID	mL of DI water added to Pb, Cu, & Zn	mL of DI water added to Cd
A	85	91
B 1 - 3	86	92
C	97	93
D	88	94
E 1 - 3	89	95
F	90	96
G	91	97
H	92	98
I 1 - 3	93	99
J	95	99.5
SB 1 - 3	100	100
MB B	86	92
MB E	89	95
MB I	93	99

3. Prepare stock solution for the selected metal using the masses listed below. Add metals to 1L volumetric and dilute with DI water. Extract 500 mL of the solution and add to a second 1L volumetric with an additional 500 mL of DI water. All stocks are made to a final concentration of 500 mg/L, so that 1ml of stock = 0.5 mg of metal. All stock solutions will be analyzed directly using the AAS.

Metal	Metal Salt	Mass - g (as metal)	Metal-g (as salt)
Lead	$Pb(NO_3)_2$	1	1.6
Cadmium	$CdCl_2$	1	1.63
Copper	$CuCl_2 \cdot 2H_2O$	1	2.69
Zinc	$ZnCl_2$	1	2.09

4. Add stock to each isotherm bottle to bring total volume to 100 mL.
5. Allow the reactor to equilibrate by shaking for 24 hours.
6. After equilibration, acidify metal blanks (MB) by adding 8 mL of HNO_3 to the reactor bottles.
7. For the following samples a Total Metal Analysis was completed to allow for determination of the mass balance closure: B1, E1, I1, SB1, SB2, and SB3.
8. Total Metal Analysis: Using a magnetic stir bar, a homogeneous 50 mL aliquot is extracted and 4 mL of HNO_3 is added. The extracted sample is shaken for 15 minutes. The sample was filtered and the filtrate analyzed on an Atomic Adsorption Spectrophotometer

9. Equilibrium concentration Analysis: Each reactor bottle was centrifuged at 300 rpm for 30 minutes. After centrifugation, 25 mL aliquot of centrate is extracted and 2 mL of HNO₃ added. They are then analyzed on the AAS.

Procedure 2.D - EPA Method 3010 - Acid Digestion of Aqueous Samples and extracts for Total Metal Analysis by FLAA or ICP Spectroscopy, *Standard Methods for Water and Wastewater Analysis*, July 1992, Environmental Protection Agency, Washington, D.C.

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for analysis by flame atomic adsorption spectroscopy (FLAA) or inductively coupled argon plasma spectroscopy (ICP). The procedure is used to determine total metals.

1.2 Samples prepared by Method 3010 may be analyzed by FLAA or ICP for the following:

Aluminum	Magnesium
*Arsenic	Manganese
Barium	Molybdenum
Beryllium	nickel
Cadmium	Potassium
Calcium	*Selenium
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

* Analysis by ICP

NOTE: See Method 7760 for the digestion and FLAA analysis for Silver.

1.3 This digestion procedure is not suited for samples which will be analyzed by graphite furnace atomic adsorption spectroscopy because hydrochloric acid can cause interferences during furnace atomization. Consult Method 3020A for samples requiring graphite furnace analysis.

2.0 SUMMARY OF METHOD

2.1 A mixture of nitric acid and the material to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is refluxed with hydrochloric acid and brought up to volume. If sample should go to dryness, it must be discarded and the sample reprepared.

3.0 INTERFERENCES

3.1 Interferences are discussed in the referring analytical method.

4.0 APPARATUS AND MATERIALS

- 4.1 Griffin beakers - 150mL or equivalent
- 4.2 Watch glasses - Ribbed or plain or equivalent
- 4.3 Qualitative filter paper or centrifugation equipment
- 4.4 Graduated cylinder - 100 ml
- 4.5 Funnel

4.6 Hot plate or equivalent heating source - adjustable and capable of maintaining a temperature of 90-95°C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents to the American Chemical society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified.

5.3 Nitric Acid. (concentrated), HNO_3 . Acid should be analyzed to determine levels of impurities. If method blank is \leq MDL, the acid can be used.

5.4 Hydrochloric Acid (1:1), HCl . Prepared from water and hydrochloric acid. Hydrochloric acid should be analyzed to determine level of impurities. If method blank is $<$ MDL, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 All samples must have been collected using a sampling plant that addresses the considerations discussed in Chapter 9

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable.

6.3 Aqueous wastewaters must be acidified to a pH of < 2 with HNO_3 .

7.0 PROCEDURE

7.1 Transfer A 100ml representative aliquot of the well-mixed sample to a 150 ml Griffin beaker and add 3 ml of concentrated HNO_3 . Cover the beaker with a ribbed watch glass or equivalent. Place the beaker on a hot plate or equivalent heating source and cautiously evaporate to a low volume (5 ml), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 3 ml portion of concentrated HNO_3 . Cover the beaker with a non ribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

NOTE: If a sample is allowed to go to dryness, low recoveries will result.

7.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color). Again, uncover the beaker and evaporate to a low volume. Cool the beaker. Add a small quantity of 1:1 HCl , cover the beaker, and reflux for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation.

7.3 Wash down the beaker walls and watch glass with water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is a concern for the clogging of the nebulizer. This additional step can cause sample contamination unless filter and apparatus are thoroughly cleaned. Rinse the filter and apparatus with dilute nitric acid. Filter the sample and adjust the final volume to 100 ml with reagent water and the final acid concentration to 10%. The sample is now ready for analysis.

MODIFICATIONS TO EPA METHOD 3010

Each sample was filtered prior to acidification and a 7 ml aliquot was placed in a Hach COD vial. Hydrochloric acid and HNO_3 were added at 5% by volume (0.350 ml). The samples were heated to 121°C in an autoclave for 20 minutes. A solution of 48% H_2O_2 was added also at 5% by volume (0.350 ml), and reheated. Each sample was then examined to determine if the humic material had been completely digested. If not, the process was repeated, and the sample examined a second time. If the particulate material still remained, 0.700 ml of the 48% H_2O_2 was added, and the sample reheated. Due to the volume of the vials used, only three digestions were capable of being performed. Generally, only ten to 15 samples could not be digested completely for each experiment. After digestion, the samples were analyzed using ICP Spectroscopy.

Procedure 3.D - Digestion of Plant Material Using HNO_3 (Havlin and Soltanpour 1981)

Collection of Sample

- Samples will be collected on an as needed basis following the initial metal migration experiment. An initial sampling will be taken to determine the background concentration of metals in the plant material.
- Samples will consist of leaf and stem material only, with the exception being that after the soil cores are taken the root will be analyzed separately from the stem and leaf material.
- Realizing that the plant material is approximately 85 to 90 % water, greater than 5 grams of clippings should be harvested.

Grinding

- The plant material must be dried in a 103°C oven for approximately 24 hours.
- using a mortar and pestle, the dried material must be ground until the average particle size is less than 1 mm in length.

Digestion (Havlin and Soltanpour 1981)

- Carefully weigh 0.5 to 1.0 grams of a WELL MIXED sample of finely ground material.
- Place weighed material into a glass graduated Taylor tube.
- Add 10 mL of concentrated HNO_3 .
- Let tube stand for 24 hours.
- After 24 hours, heat samples to 125°C in a hot oil bath under a fume hood for 4 hours and cool.
- Dilute to 12.5 mL with concentrated HNO_3 .
- Dilute to 50 mL with deionized water.
- Mix well and allow any solid matter to settle.

Analysis

- Filter samples to remove any remaining cellulose
- All samples will be analyzed using an Atomic Adsorption Spectrophotometer.

References

Havlin, J.L. and P.N. Soltanpout. 1981. 'A nitric acid plant tissue digest method for use with inductively coupled plasma spectroscopy.' Agronomy Abstracts. p. 178.